Access DB# 215056

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: LEE, RIP A. Examiner #: 78680 Date: 02-07-2007
Art Unit: 1713 Phone Number 1104 Serial Number: 10/500,543
Mail Box and Bldg/Room Location: ~~RR~~ 10A21 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

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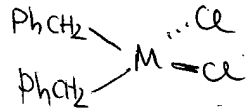
Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: PREPARATION of DIALKYL-ANSA-METALLOCENES

Inventors (please provide full names): SCHOTTEK J.
SCHAUER, D.

Earliest Priority Filing Date: JAN 08 - 2002

**For Sequence Searches Only* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.*

Please search for use of  in preparation of metallocenes †

M = Ti, Zr, Hf

sample nomenclature:

dibenzyl dichloro zirconium
dichloro zirconium dibenzyl
dibenzyl zirconium dichloride

and permutations thereof

† any metallocene or metallocene type ie, Cp, Indenyl, Fluorenyl

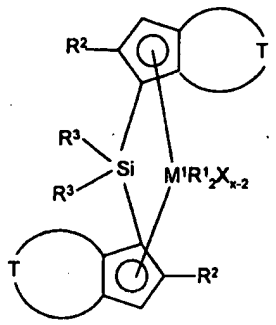
****

STAFF USE ONLY	Type of Search		Vendors and cost where applicable	
Searcher: EJ	NA Sequence (#)		STN	
Searcher Phone #:	AA Sequence (#)		Dialog	
Searcher Location:	Structure (#)		Questel/Orbit	
Date Searcher Picked Up:	Bibliographic		Dr.Link	
Date Completed: 2-9-07	Litigation		Lexis/Nexis	
Searcher Prep & Review Time:	Fulltext		Sequence Systems	
Clerical Prep Time:	Patent Family		WWW/Internet	
Online Time:	Other		Other (specify)	

PTO-1590 (8-01)

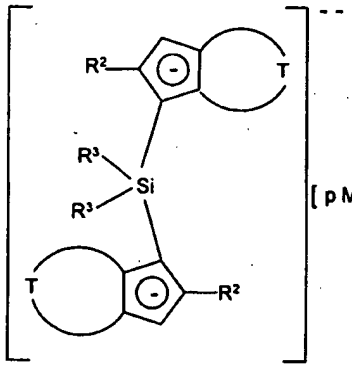
AMENDMENTS TO THE CLAIMS

1. (currently amended) A process for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I)



(I)

which comprises reacting a ligand starting compound of the formula (II)



(II)

with a transition metal dialkyl compound of the formula (III)

$$M^1X_xR^1{}_2{}^*D_y \quad (III),$$

where

M^1 is an element of group 4, 5 or 6 of the Periodic Table of the Elements[[,]];

R^1 are identical C_1-C_{20}-alkyl or C_7-C_{40}-arylalkyl radicals[[,]];

X are identical or different halogens[[,]];

R^2 are identical or different C_1-C_{40} radicals[[,]];

R^3 are identical or different C_1-C_{40} radicals[[,]];

T is a divalent C_1-C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12 atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring[[,]];

M^2 is Li, Na, K, MgCl, MgBr, MgI, Mg or Ca[[,]];

D is an uncharged Lewis base ligand[[,]];

x is equal to the oxidation number of M^1 minus 2[[,]];

y is from 0 to 2;

and

p is 1 in the case of doubly positively charged metal ions or 2 in the case of singly positively charged metal ions or metal ion fragments.

2. (currently amended) ~~A~~The process as claimed in claim 1, wherein

T is a 1,3-butadiene-1,4-diyl group which may be unsubstituted or be substituted by from 1 to 4 radicals R^4, where the two 1,3-butadiene-1,4-diyl groups may be different[[,]];

R^4 are identical or different C_1-C_{20} radicals[[,]];

M^1 is titanium, zirconium or hafnium[[,]];

R^1 are identical C_1-C_5-alkyl or C_7-C_{20}-arylalkyl radicals[[,]]; and

X is halogen ~~and~~

~~R^2, R^3, M^2, D, p, x and y are as defined in claim 1~~.

3. (currently amended) ~~A~~The process as claimed in claim 1 ~~or 2~~, wherein the transition metal dialkyl compound of the formula (III) is produced at above –30°C by combining a compound M^1X_{x+2} with from 2 to 2.5 equivalents of a compound R^1M^3 in the presence of a ligand compound D, where

M^3 is Li^+, Na^+, K^+, $MgCl^+$, $MgBr^+$, MgI^+, ½ [Mg^{++}] or ½ [Zn^{++}], ~~and~~

~~the other variables are as defined in claim 1 or 2~~.

4. (currently amended) ~~A~~The process as claimed in claim 1 ~~or 2~~, wherein the ligand starting compound of the formula (II) ~~or (V)~~ is combined with the transition metal dialkyl compound of the formula (III) at above –30°C.

5. (currently amended) ~~A~~The process as claimed in claim 4, wherein ~~the~~a reaction mixture is maintained at from 30°C to 150°C for a period of at least 10 minutes after the reaction components have been combined.

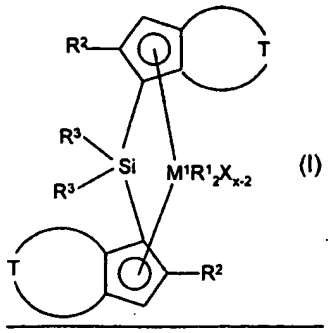
6. (currently amended) ~~A~~The process as claimed in ~~any of claims~~claim 1 ~~to 5~~, wherein the reaction is carried out in an organic solvent or solvent mixture which comprises at least 10% by volume of an ether.

7. (currently amended) ~~A~~The process as claimed in ~~any of claims~~claim 1 ~~to 6~~, wherein ~~the~~a racemoselectivity = (proportion of rac – proportion of meso)/(proportion of rac + proportion of meso) is greater than zero.

8. (currently amended) ~~The use of~~A process comprising utilizing a transition metal dialkyl compound of the formula (III):

$$M^1X_xR^1_2{*}D_y \quad \text{(III)}$$

for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I):



(I)

wherein

M^1 is an element of group 4, 5 or 6 of the Periodic Table of the Elements;

R^1 are identical C_1-C_{20}-alkyl or C_7-C_{40}-arylalkyl radicals;

X are identical or different halogens;

R^2 are identical or different C_1-C_{40} radicals;

R^3 are identical or different C_1-C_{40} radicals;

D is an uncharged Lewis base ligand;

y is from 0 to 2;

T is a divalent C_1-C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12 atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring; and

x is equal to the oxidation number of M^1 minus 2.

9. (new) The process as claimed in claim 2, wherein the transition metal dialkyl compound of the formula (III) is produced at above –30°C by combining a compound M^1X_{x+2} with from 2 to 2.5 equivalents of a compound R^1M^3 in the presence of a ligand compound D, where

M^3 is Li^+, Na^+, K^+, $MgCl^+$, $MgBr^+$, MgI^+, ½ [Mg^{++}] or ½ [Zn^{++}].

10. (new) The process as claimed in claim 2, wherein the ligand starting compound of the formula (II) is combined with the transition metal dialkyl compound of the formula (III) at above –30°C.

11. (new) The process as claimed in claim 10, wherein a reaction mixture is maintained at from 30°C to 150°C for a period of at least 10 minutes after the reaction components have been combined.

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Bib Data Sheet

CONFIRMATION NO. 6726

SERIAL NUMBER	FILING OR 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/500,543	12/20/2004 RULE	525	1712	LU 6001 (US)

APPLICANTS

Jorg Schottek, Frankfurt, GERMANY;
Diana Schauer, Bruchkobel, GERMANY;

**** CONTINUING DATA ***************************

This application is a 371 of PCT/EP02/14379 12/17/2002

**** FOREIGN APPLICATIONS *********************

GERMANY 102 00 422.6 01/08/2002

Foreign Priority claimed	STATE OR COUNTRY	SHEETS DRAWING	TOTAL CLAIMS	INDEPENDENT CLAIMS
☐ yes ☐ no 35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance Verified and Acknowledged _____ Examiner's Signature Initials	GERMANY		11	2

ADDRESS

34872

TITLE

Preparation of dialkyl-ansa-metallocenes

FILING FEE RECEIVED		
1050	FEES: Authority has been given in Paper No. _____ to charge/credit DEPOSIT ACCOUNT No. _____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

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L6           10 S L5 AND RSD/FA
L7           28 S L5 NOT L6

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L9           19 S L7

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L11         124 S L7
L12          40 S L7 (L) RACT/RL
L13       18113 S ?METALLOCEN? OR ?METALOCEN?
L14           6 S L11 AND L13
L15          36 S L12 NOT L14
L16           4 S L12 AND L14
L17           6 S L14 OR L16
L18          28 S 1840-2002/PY,PRY AND L10
L19         105 S 1840-2002/PY,PRY AND L11
L20           6 S L17 AND L19
L21          27 S L15 AND L19

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L22          46 S ?METALLOCEN? OR ?METALOCEN?
L23           0 S L9 AND L22

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      |
      2
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1   |   3                     @9  10
    |
    G1
    12

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VAR G2=15/18/21
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CONNECT IS E2  RC AT   9
CONNECT IS E1  RC AT  10
CONNECT IS E4  RC AT  15
CONNECT IS E4  RC AT  18
CONNECT IS E4  RC AT  21
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GGCAT   IS SAT  AT   9
GGCAT   IS UNS  AT  10
DEFAULT ECLEVEL IS LIMITED

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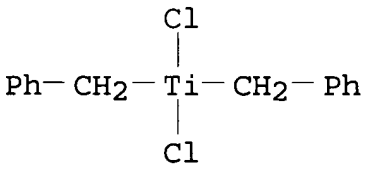
=> D L18 1-28 CBIB ABS HITSTR HITRN

L18 ANSWER 1 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:174636 Polymerization processes using volatile hydrofluorocarbon diluents. McDonald, Michael F.; Milner, Scott T.; Shaffer, Timothy D.; Webb, Robert N. (Exxonmobil Chemical Patents Inc., USA). PCT Int. Appl. WO 2004067577 A2 20040812, 130 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US41221 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464187P 20030421; US 2003-479081P 20030617.

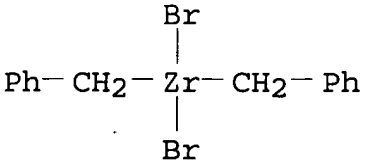
AB A polymn. process comprising contacting a catalyst system, a diluent comprising one or more hydrofluorocarbon(s) (HFC's), and one or more monomer(s) to form a polymn. medium, wherein the polymn. medium is evapd. during the polymn. The invention provides for polymn. processes to produce polymers utilizing boiling pool reactor systems and diluents including hydrofluorocarbons. The process was used in polymn. of isobutylene and isoprene in the presence of MeF.

IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(polymn. processes using volatile hydrofluorocarbon diluents)

RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**

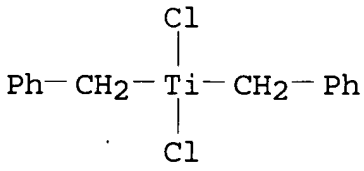
, Dibenzylzirconium dibromide
(polymn. processes using volatile hydrofluorocarbon diluents)

L18 ANSWER 2 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:124920 Copolymers with new sequence distributions and blends. Shaffer, Timothy D.; Chung, David Y. (Exxonmobil Chemical Patents Inc., USA). PCT Int. Appl. WO 2004058836 A1 20040715, 133 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US40916 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464187P 20030421; US 2003-479081P 20030617.

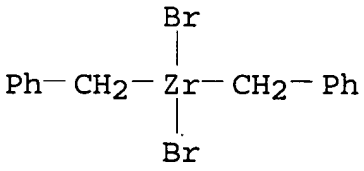
AB The polymn. processes include diluents including hydrofluorocarbons to produce novel polymers with new sequence distributions. In particular, the copolymers of an isoolefin, preferably isobutylene, and a conjugated diene, more preferably isoprene, show new sequence distributions.

IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(butyl rubber with a particular isoolefin-isoprene triad sequence distribution)

RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**

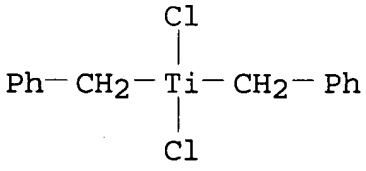
, Dibenzylzirconium dibromide
(butyl rubber with a particular isoolefin-isoprene triad sequence distribution)

L18 ANSWER 3 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:124919 Copolymers substantially free of long chain branching and blends. Milner, Scott T.; Shaffer, Timothy D.; Chung, David Y. (Exxonmobil Chemical Patents Inc., USA). PCT Int. Appl. WO 2004058835 A1 20040715, 130 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US40341 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464187P 20030421; US 2003-479081P 20030617.

AB The polymn. processes include diluents of hydrofluorocarbons to produce novel polymers substantially free of long chain branching. In particular, the copolymers of an isoolefin, preferably isobutylene, and a conjugated diene, more preferably isoprene, are substantially free of long chain branching.

IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(butyl rubber substantially free of long chain branching and agglomeration)

RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
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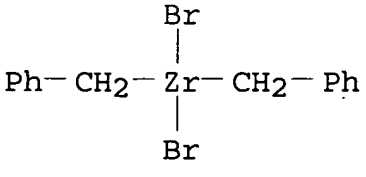


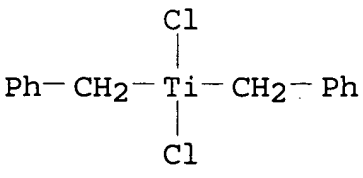
IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(butyl rubber substantially free of long chain branching and agglomeration)

L18 ANSWER 4 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:124144 Polymerization processes utilizing bayonet cooled slurry reactor systems and diluents including hydrofluorocarbons.
Mcdonald, Michael F.; Milner, Scott T.; Shaffer, Timothy D.; Webb, Robert N. (Exxonmobil Chemical Patents, Inc., USA). PCT Int. Appl. WO 2004058829 A1 20040715, 128 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US40858 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464187P 20030421; US 2003-479081P 20030617.

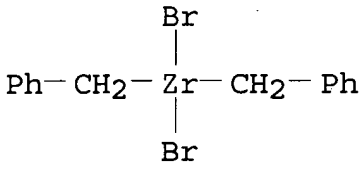
AB The invention relates to new polymn. processes to produce polymers utilizing bayonet cooled slurry reactor systems and diluents comprising hydrofluorocarbons. In particular, the invention provides for a process to produce polymers comprising contacting one or more monomer(s), e.g., isobutylene, a catalyst system, and a diluent comprising one or more hydrofluorocarbon(s) (HFC's) in a reactor comprising a bayonet.

IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(polymn. process utilizing bayonet cooled slurry reactor systems and diluents including hydrofluorocarbons)

RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(polymn. process utilizing bayonet cooled slurry reactor systems and diluents including hydrofluorocarbons)

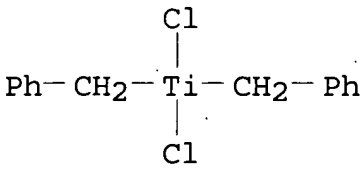
L18 ANSWER 5 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:124143 Polymerization processes utilizing a hydrofluorocarbon diluent. Shaffer, Timothy D.; Milner, Scott T.; Matturro, Michael G.; Chung, David Y.; Mcdonald, Michael F.; Webb, Robert N. (Exxonmobil Chemical Patents Inc., USA). PCT Int. Appl. WO 2004058828 A1 20040715, 119 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US40903 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464187P 20030421; US 2003-464261P 20030421; US 2003-479081P 20030617; US 2003-479136P 20030617.

AB The invention provides for a process to produce polymers utilizing a hydrofluorocarbon diluent. In one embodiment, the invention provides a polymn. medium suitable to polymerize one or more monomer(s) to form a polymer, the polymn. medium comprising one or more Lewis acid (s) and a diluent comprising one or more hydrofluorocarbon(s) (HFC); wherein the one or more Lewis acid (s) is not a compd. represented by formula MX3, where M is a group 13 metal and X is a halogen. In a preferred embodiment, the polymn. process produces polymers that include (poly)isobutylene homopolymers, isobutyleneisoprene (butyl rubber) copolymers, isobutylene and alkylstyrene copolymers, and star-branched butyl rubber terpolymers.

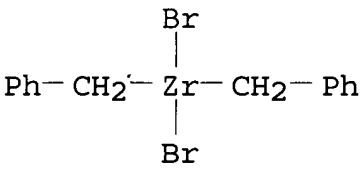
IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(polymn. processes utilizing hydrofluorocarbon diluent contg. Lewis acid)

RN 85412-32-4 ZCA

CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**
, Dibenzylzirconium dibromide
(polymn. processes utilizing hydrofluorocarbon diluent contg. Lewis acid)

L18 ANSWER 6 OF 28 ZCA COPYRIGHT 2007 ACS on STN
141:124142 Polymerization processes utilizing a hydrofluorocarbon diluent. Milner, Scott T.; Matturro, Michael G.; Shaffer, Timothy D.; Webb, Robert N.; Chung, David Y.; Mcdonald, Michael F. (Exxonmobil Chemical Patents Inc., USA). PCT Int. Appl. WO 2004058827 A1 20040715, 117 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2003-US40340 20031219. PRIORITY: US 2002-435061P 20021220; US 2003-464268P 20030421; US 2003-464283P 20030421; US 2003-479137P 20030617; US 2003-479082P 20030617.

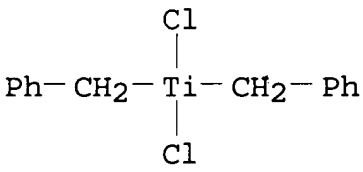
AB The invention provides for a process to produce polymers utilizing a hydrofluorocarbon diluent. In one embodiment, the invention provides a polymn. medium suitable to polymerize one or more monomer(s) to form a polymer, the polymn. medium comprising one or more Lewis acid (s) and a diluent comprising one or more hydrofluorocarbon(s) (HFC); wherein the one or more Lewis acid (s) is not a compd. represented by formula MX3, where M is a group 13 metal and X is a halogen. In a preferred embodiment, the polymn.

process produces polymers that include (poly)isobutylene homopolymers, isobutyleneisoprene (butyl rubber) copolymers, isobutylene and alkylstyrene copolymers, and star-branched butyl rubber terpolymers.

IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**, Dibenzylzirconium dibromide
(polymn. processes utilizing hydrofluorocarbon diluent contg. Lewis acid)

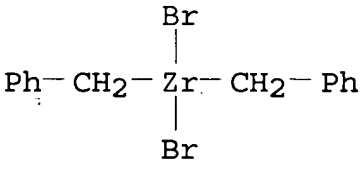
RN 85412-32-4 ZCA

CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA

CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



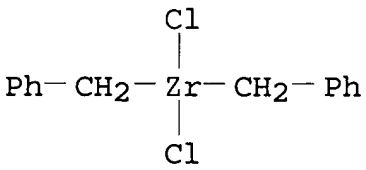
IT **85412-32-4**, Dibenzyltitanium dichloride **108816-02-0**, Dibenzylzirconium dibromide
(polymn. processes utilizing hydrofluorocarbon diluent contg. Lewis acid)

L18 ANSWER 7 OF 28 ZCA COPYRIGHT 2007 ACS on STN

138:14191 Surprising activity for Group 4 polyolefin catalysts [M{(OAr)2py}Cl2(thf)] (M = Zr, Ti) bearing tridentate pyridine-2,6-bis(aryloxide) ligands. Chan, Michael C. W.; Tam, Ka-Ho; Pui, Yung-Lin; Zhu, Nianyong (Department of Chemistry and HKU-CAS Joint Laboratory for New Materials, The University of Hong Kong, Hong Kong SAR, Peop. Rep. China). Journal of the Chemical Society, Dalton Transactions (16), 3085-3087 (English) **2002**. CODEN: JCSDAA. ISSN: 1472-7773. Publisher: Royal Society of Chemistry.

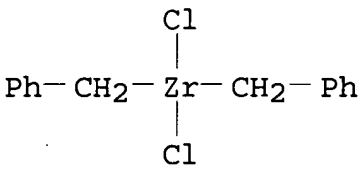
AB Unexpectedly high polymn. activity of ethylene was obsd. for zirconium (IV) catalysts supported by a rigid tridentate pyridine-bis(phenolate) ligand in conjunction with MAO; a methodol. towards analogs with unsym. ligands and the significance of the coordinated solvent mol. are described.

IT **24356-03-4**, Dibenzyldichlorozirconium
(high activity of zirconium and titanium olefin polymn. catalysts bearing tridentate pyridine-2,6-bis(aryloxide) ligands)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzyldichlorozirconium
(high activity of zirconium and titanium olefin polymn. catalysts bearing tridentate pyridine-2,6-bis(aryloxide) ligands)

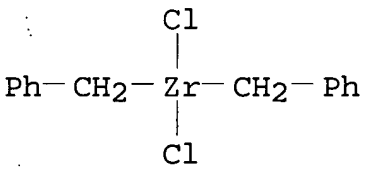
L18 ANSWER 8 OF 28 ZCA COPYRIGHT 2007 ACS on STN
134:311280 Zirconium Complexes of Fluorinated Aryl Diamides. O'Connor, Paul E.; Morrison, Darryl J.; Steeves, Sheryl; Burrage, Katherine; Berg, David J. (Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6, Can.). Organometallics, 20(6), 1153-1160 (English) **2001.** CODEN: ORGND7. ISSN: 0276-7333. OTHER SOURCES: CASREACT 134:311280. Publisher: American Chemical Society.
AB The reaction of excess ArFNHLi with (ICH2CH2OCH2)2 affords the new diamines (ArFNHCH2CH2OCH2)2 (1, ArF = C6F5; 2, ArF = 3,5-C6H3(CF3)2) in moderate yield. Direct protonolysis of Zr(CH2Ph)nCl4-n (n = 2-4) or Zr[N(SiMe3)2]nCl4-n (n = 2, 3) with 1 or 2 (1 equiv.) affords the zirconium complexes Zr(ArFNCH2CH2OCH2)2(X)(Y) (ArF = C6F5: 3, X = Y = Cl; 4, X = N(SiMe3)2, Y = Cl; 5, X = Cl, Y = CH2Ph; 6, X = Y = CH2Ph. ArF = 3,5-C6H3(CF3)2: 7, X = Y = Cl; 8, X = Y = CH2Ph). The structures of 1, 4, 5, and 7 were established by x-ray crystallog. with the zirconium complexes 4, 5, and 7 all adopting a monocapped trigonal bipyramidal geometry in the solid state. However, in soln., these complexes display higher symmetry due to rapid ligand rearrangement. The silylamido complex 4 shows restricted rotation of the C6F5 rings in soln. ($\Delta G^{\ddagger}$thermod. = 49 ± 3 kJ mol-1). Abstraction of a benzyl group from 6 by B(C6F5)3 affords {Zr[CH2OCH2CH2N(C6F5)]2(CH2Ph)}+{(PhCH2)B(C6F5)3}- (9). This complex shows evidence for η2-benzyl coordination and does not polymerize ethylene at room temp. Treatment of 3 with excess MAO (500 equiv) and ethylene (1 atm, 50°) affords polyethylene at a modest rate (3.2 kg mol-1 Zr h-1).
IT **24356-03-4**, Dibenzyldichlorozirconium
(protonolysis with fluorinated aryl diamides)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzyldichlorozirconium
(protonolysis with fluorinated aryl diamides)

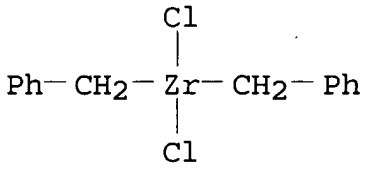
L18 ANSWER 9 OF 28 ZCA COPYRIGHT 2007 ACS on STN
130:139675 Ethylene Polymerization with Dimeric Zirconium and Hafnium Silsesquioxane Complexes. Duchateau, Robbert; Abbenhuis, Hendrikus C. L.; van Santen, Rutger A.; Meetsma, Auke; Thiele, Sven K.-H.; van Tol, Maurits F. H. (Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, 5600 MB, Neth.). Organometallics, 17(26), 5663-5673 (English) **1998**. CODEN: ORGND7. ISSN: 0276-7333. Publisher: American Chemical Society.
AB Treatment of the silanol (c-C5H9)7Si8O12(OH) with Cp''Ti(CH2Ph)3 (Cp'' = 1,3-C5H3(SiMe3)2) or TiCl4 selectively affords the mono(silsesquioxane) complexes Cp''[(c-C5H9)7Si8O13]Ti(CH2Ph)2 and [(c-C5H9)7Si8O13]TiCl3, resp., while with M(CH2Ph)4 (M = Ti, Zr, Hf) mixts. of products were obtained. When the disilanol (c-C5H9)7Si7O9(OSiMe3)(OH)2 is reacted with M(CH2Ph)4 (M = Ti, Zr), the bis(silsesquioxane) complexes [(c-C5H9)7Si7O11(OSiMe3)]2M (M = Ti (I), Zr (II), Zr·2THF (III)) are formed exclusively. With (PhCH2)2ZrCl2·OEt2 as precursor, the mono(silsesquioxane) complex [(c-C5H9)7Si7O11(OSiMe3)]ZrCl2·2THF can be isolated. M(CH2Ph)4 (M = Ti, Zr, Hf) reacts smoothly with the tris(silanol) (c-C5H9)7Si7O9(OH)3, giving the metallasilsesquioxane benzyl species, {[(c-C5H9)7Si7O12]MCH2Ph}n (M = Ti, n = 1 (IV); M = Zr, n = 2 (V); M = Hf, n = 2 (VI)). Compds. III and V were characterized by X-ray anal. Dimer V consists of a zwitterionic-like structure with 2 electronically different metal sites. M-C bond hydrogenolysis of V and VI affords the corresponding hydrides, which are active α-olefin hydrogenation catalysts. Without cocatalyst, the neutral dimers V and VI are poor, though active, ethylene polymn. catalysts (activity: (5-10) + 103 g PE/(mol·h)). Addn. of B(C6F5)3 affords the cationic, mono(benzyl) complexes {[(c-C5H9)7Si7O12]2M2(CH2Ph)}(+) (M = Zr, Hf): single-site catalysts (activity: (2-8) + 106 g PE/(mol·h)) that are considerably more active than the neutral V and VI. Whereas titanasilsesquioxanes I and IV do not react with THF, the corresponding zirconasilsesquioxanes II and V form bis(THF) adducts, III and [(c-C5H9)7Si7O12]ZrCH2Ph·2THF, which suggests that the Ti complexes are less electrophilic than the Zr ones. Accordingly, the titanium complex IV does not react with dihydrogen and is inactive in ethylene polymn. 200870-69-5.

IT **24356-03-4**, Dibenzyldichlorozirconium
(starting material; ethylene polymn. and olefin hydrogenation with dimeric zirconium and hafnium silsesquioxane complexes)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



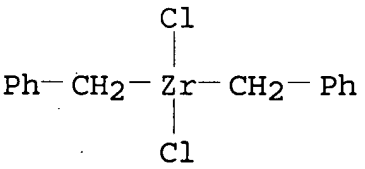
IT **24356-03-4**, Dibenzyldichlorozirconium
(starting material; ethylene polymn. and olefin hydrogenation with dimeric zirconium and hafnium silsesquioxane complexes)

L18 ANSWER 10 OF 28 ZCA COPYRIGHT 2007 ACS on STN
126:317451 Cationic Zirconium Dialkyl and Alkyl Complexes Supported by DAC (Deprotonated 4,13-Diaza-18-crown-6) Ligation. Lee, Lawrence; Berg, David J.; Bushnell, Gordon W. (Department of Chemistry, University of Victoria, Victoria, BC, 3065, Can.). Organometallics, 16(12), 2556-2561 (English) **1997.** CODEN: ORGND7. ISSN: 0276-7333. OTHER SOURCES: CASREACT 126:317451. Publisher: American Chemical Society.
AB The synthesis, characterization, and reactivity of neutral and cationic Zr alkyls supported by DAC (deprotonated 4,13-diaza-18-crown-6) ligation are reported. Reaction of H2DAC with Zr(CH2Ph)4 affords a 1:4 mixt. of cis- and trans-Zr(DAC)(CH2Ph)2 (cis-/trans-1a). The pure isomers undergo slow cis-trans isomerization in soln. to regenerate the 1:4 cis:trans equil. mixt. X-ray crystallog. results are reported for both cis- and trans-1a. Reaction of Zr(CH2Ph)2Cl2 with H2DAC, followed by treatment with LiR (2 equiv), gives cis-Zr(DAC)R2 (R = CH2SiMe3, cis-1b; R = CH2CMe3, cis-1c) exclusively. Alkyl abstraction from cis- or trans-1a using B(C6F5)3 (1 equiv) produces the stable cation [Zr(DAC)(CH2Ph)]+[B(CH2Ph)(C6F5)3]- (2a) as a yellow oil. NMR studies on 2a in CD2Cl2 show no evidence for η2-benzyl formation or anion coordination. Protonation of cis- or trans-1a with [Bu3NH]+[BPh4]- similarly yields [Zr(DAC)(CH2Ph)]+[BPh4]- (2b). Cation 2a reacts with t-BuNC to form the vinyl amide complex [Zr(DAC){N(t-Bu)CH:CHPh}]+[B(CH2Ph)(C6F5)3]- (3). P-Tolylacetylene undergoes catalytic dimerization to (Z)-1,4-di-p-tolyl-1-buten-3-yne in the presence of 2a.
IT **24356-03-4**, Dibenzyldichlorozirconium
(reaction with diaza-18-crown-6)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzyldichlorozirconium
(reaction with diaza-18-crown-6)

L18 ANSWER 11 OF 28 ZCA COPYRIGHT 2007 ACS on STN
123:199699 Catalysts for olefin polymerization. Aida, Fuyuki; Tajima, Yoshio; Matsura, Kazuo (Nippon Oil Co Ltd, Japan). Jpn. Kokai Tokkyo Koho JP 07133307 A **19950523** Heisei, 19 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-310982 19931108.
AB The title polymn. catalyst contains M1R1p(OR2)qX14-p-q [R1, R2 = C1-24 hydrocarbyl; X1 = halo, M1 = Zr, Ti, Hf; 0≤p≤4; 0≤q≤4, 0<p+q≤4], M2R3m(OR4)nX2z-m-n [R3, R4 = C1-24 hydrocarbyl; X2 = halo, M2 = Group I-III element; z = valence of M2; 0≤n≤z; 0≤m≤z; 0≤m+n≤z], cyclic compd. contg. ≥2 conjugated double bonds, and a sulfide. High mol. wt. polyolefins can be obtained with relatively wide mol. wt. distribution and polyolefins can be obtained in high yield with minimal use of a modified org. Al.
IT **24356-03-4**, Dibenzylzirconium dichloride
(olefin polymn. catalyst contg.)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzylzirconium dichloride
(olefin polymn. catalyst contg.)

L18 ANSWER 12 OF 28 ZCA COPYRIGHT 2007 ACS on STN
123:84301 Olefin polymerization catalyst components. Aida, Fuyuki; Tajima, Yoshio; Matsuura, Kazuo (Nippon Oil Co. Ltd., Japan). PCT Int. Appl. WO 9511928 A1 **19950504**, 27 pp. DESIGNATED STATES: W: CA, DE, US. (Japanese). CODEN: PIXXD2. APPLICATION: WO 1994-JP1813 19941027. PRIORITY: JP 1993-302148 19931027; JP 1994-164448 19940614.

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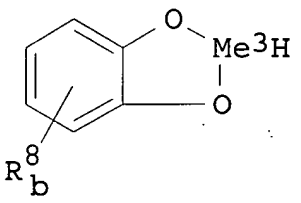


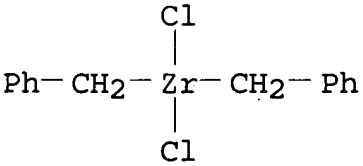
I

AB The title component is prepd. by contacting the following compds. (1) Me1R1p(OR2)qX14-p-q, where R1 and R2 are independently C1-24 hydrocarbyl; X is halogen; Me is Zr, Ti of Hf; and p and q are integers satisfying the conditions 0≤p≤4, 0≤q≤4, 0≤p+q≤4; (2) at least one of (a) Me2R3m(OR)mX2z-m-n, (b) Me3HzR53-a, (c) Me4[Me3HbR6c(OR7)4-b-c]y, and (d) I wherein R3, R4, R5, R6, R7 and R8 may be the same of different and each represents C1-24 hydrocarbyl; Me2 represents a group 1, 2, 12, or 13 element of the Periodic Table; M3 represents a Group 13 element thereof; M34 represents a Group 1, 2, or 12 element thereof; X2 represents halogen; z represents the valency of Me2; y represents the valency of Me4; and m, n, a, b, c and d are integer s satisfying the conditions 0≤m≤z, 0≤n≤z, 0≤m+n≤z, 0≤a≤3, 1≤b≤4, 1≤c≤3, 1≤b+c≤4, and 0≤d≤4; (3) a cyclic org. compd. having at least two conjugated double bonds; and (4) a compd. having a carbon-halogen linkage. The component is useful for producing an olefin polymer having a high mol. wt. and a relatively wide mol. wt. distribution in a high yield using a reduced amt. of a modified organoaluminum compd. such as Me aluminoxane. 1-Butene and ethylene were copolymd. using a catalyst prepd. from tetrabutoxyzirconium, trihexylaluminum, 1,2-bis(indenyl)ethane, 2,2,2-trifluoroethyl trityl ether, and Me aluminoxane.

IT **24356-03-4**, Dibenzylzirconium dichloride
(olefin polymn. catalyst components)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzylzirconium dichloride
(olefin polymn. catalyst components)

L18 ANSWER 13 OF 28 ZCA COPYRIGHT 2007 ACS on STN
123:10195 Use of titanium and zirconium compounds as homogeneous catalyst and novel titanium and zirconium compounds. Schaverien, Colin John; Van Der Linden, Adrianus Johann (Shell Internationale Research Maatschappij B. V., Neth.). Eur. Pat. Appl. EP 606125 A2 **19940713**, 12 pp. DESIGNATED STATES: R: DE, FR, GB. (English). CODEN: EPXXDW. APPLICATION: EP 1994-200025 19940106. PRIORITY: EP 1993-200046 19930108.

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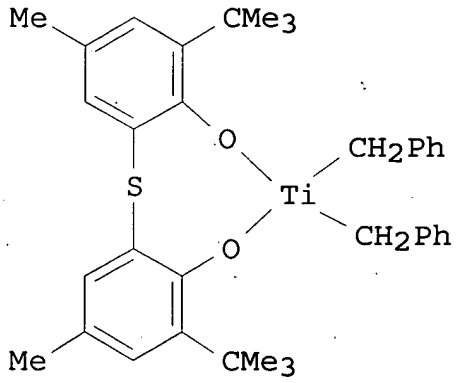


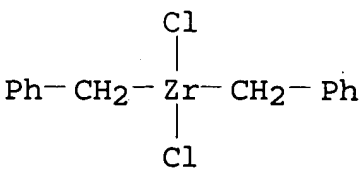
I

AB The title compds. are prepd. from 2,2'-dihydroxy-1,1'-biphenyls and 2,2'-dihydroxy-1,1'-binaphthyls and used as homogeneous catalysts in the polymn. and oligomerization of unsatd. hydrocarbons (e.g., ethylene, propene, 1-hexene, and butadiene) and the cyclic trimerization of compds. contg. an ethynyl group. A catalyst I was prepd. from bis(3-tert-butyl-2-hydroxy-5-methylphenyl) sulfide and Ti(CH2Ph)4 and used with Me aluminoxane for the polymn. of ethylene.

IT **24356-03-4**, Dibenzylzirconium dichloride
(reaction with o,o'-dihydroxybinaphthyl derivs.)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**, Dibenzylzirconium dichloride
(reaction with o,o'-dihydroxybinaphthyl derivs.)

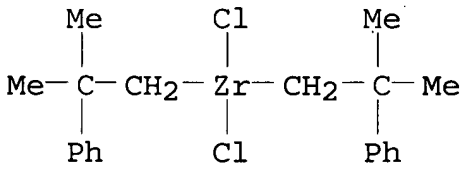
L18 ANSWER 14 OF 28 ZCA COPYRIGHT 2007 ACS on STN
113:133057 Polymerization catalysts for olefins. Saito, Noriaki; Kumahara, Katsumi (Chisso Corp., Japan). Eur. Pat. Appl. EP 366290 A2 **19900502**, 12 pp. DESIGNATED STATES: R: BE, DE, FR, GB, IT. (English). CODEN: EPXXDW. APPLICATION: EP 1989-310165 19891004. PRIORITY: JP 1988-267854 19881024.

AB Polymn. catalysts with high activity and suitable for repeated use contain liq. Group IVB transition metal compds. and aluminoxanes. Thus, polymn. of C3H6 (total pressure 3 kg/cm3) by using 1.6 mmol methylaluminoxanes (mol.-wt. 700) and 0.001 mmol ethylenebis(indenyl)zirconium dichloride in 700 mL PhMe at 50° for 2 h gave a polymer having wt.-av. mol.-wt. 25,000. This catalyst compns. was repeatedly used for 5 times with av. catalyst activity 201 + 106 g polymer/mol-Zr and 163 g/g-aluminoxane.

IT **89820-55-3**
(polymn. catalyst, for olefins)

RN 89820-55-3 ZCA

CN Zirconium, dichlorobis(2-methyl-2-phenylpropyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **89820-55-3**
(polymn. catalyst, for olefins)

L18 ANSWER 15 OF 28 ZCA COPYRIGHT 2007 ACS on STN
111:115935 New catalysts for the polymerization of olefins. Albizzati, Enrico; Resconi, Luigi Maria (Ausimont S.r.l., Italy; Himont, Inc.; Montedison S.p.A.). Eur. Pat. Appl. EP 318048 A2 **19890531**, 6 pp. DESIGNATED STATES: R: BE, DE, ES, FR, GB, NL, SE. (English). CODEN: EPXXDW. APPLICATION: EP 1988-119800 19881128. PRIORITY: IT 1987-41013 19871127.

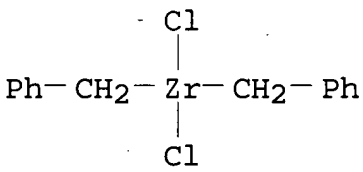
AB The highly productive title catalysts comprise a compd. of transition metals contg. ≥1 metal-halogen linkage, supported on Mg halide in the active form, and contain a compd. of Ti, Zr, or Hf having ≥1 metal-carbon linkage. A catalyst component was prepd. by adding MgCl2.3EtOH dropwise to TiCl4, heating to 100°, filtering, adding fresh TiCl4, heating the intermediate

at 120° for 2 h, and rinsing with heptane. A mixt. of C2H4 and C3H6 was polymd. in the presence of the catalyst and Zr(CH2Ph)4, producing a copolymer with catalyst productivity 2500 g/g, crystallinity 3%, and C3H6 content 40.4%.

IT **24356-03-4**
(catalysts, for polymn. of olefins)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**
(catalysts, for polymn. of olefins)

L18 ANSWER 16 OF 28 ZCA COPYRIGHT 2007 ACS on STN

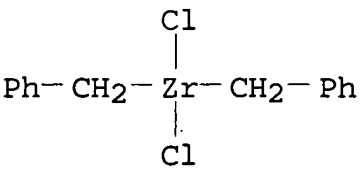
109:191060 Process and catalysts for producing crystalline vinyl aromatic polymers having a predominantly syndiotactic structure. Albizatti, Enrico; Giannini, Umberto; Giunchi, Giovanni; Mazzocchi, Romano; Resconi, Luigi (Montedison S.p.A., Italy). Eur. Pat. Appl. EP 272584 A2 **19880629**, 9 pp. DESIGNATED STATES: R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE. (English). CODEN: EPXXDW. APPLICATION: EP 1987-118572 19871215. PRIORITY: IT 1986-41007 19861215; IT 1986-22827 19861223.

AB Vinyl arom. monomers are (co)polymd. using catalysts comprising reaction products of non-titanium transition metal compds. (contg. ≥1 M-O, MC, M-N, M-P, M-S, or M-halogen bond; M = metal) and an org. Al compd. contg. ≥1 O atom bonded to Al. Styrene (30 mL) was mixed with a mixt. of 150 mg Me aluminoxane, 10 mL PhMe, and 5 mg Zr(CH2Ph)4, heated to 50° in 30 min, and polymd. 4 h, giving 20% conversion to a polymer with mol. wt. 23,000, m.p. 270°, and residue after MEK extn. 23%.

IT **24356-03-4**
(catalysts, with aluminoxanes, for prepn. of syndiotactic vinyl arom. compd. polymers)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



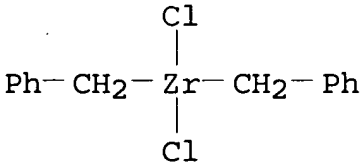
IT **24356-03-4**
(catalysts, with aluminoxanes, for prepn. of syndiotactic vinyl arom. compd. polymers)

L18 ANSWER 17 OF 28 ZCA COPYRIGHT 2007 ACS on STN
107:96822 NMR-spectroscopic investigations on the constitution of benzyl and 1-naphthylmethyl compounds of titanium, zirconium and hafnium. Scholz, Joachim; Schlegel, Michael; Thiele, Karl Heinz (Sekt. Chem., Tech. Hochsch. "Carl Schorlemmer", Merseburg, DDR-4200, Ger. Dem. Rep.). Chemische Berichte, 120(8), 1369-74 (German) **1987.** CODEN: CHBEAM. ISSN: 0009-2940. OTHER SOURCES: CASREACT 107:96822.

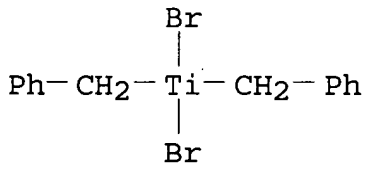
AB The 1H and 13C NMR spectra of (PhCH2)4M [M = Ti (I), Zr (II), Hf (III)] and the analogous 1-naphthylmethyl derivs. (1-C10H7CH2)4M [M = Ti, Zr, Hf (IV)] do not show noticeable changes in their bonding properties which were postulated on the basis of x-ray anal. of I-III. Substitution of benzyl groups in I and II with halide gave (PhCH2)4-nMXn (X = Cl, Br, I), in which the δCH2 values indicate the alternation of electron d. at the metal atoms. In contrast, no alternation of the benzyl group-metal bonds is indicated by the chem. shifts of the Ph group C and H atoms, but it becomes evident when benzyl groups are substituted by Cp. Whereas in I-III a η4-coordination of the benzyl groups can be assumed, these groups are η1-bonded in Cp2Ti(CH2Ph)2 and Cp2Zr(CH2Ph)2. Furthermore, an alternation of the coordination systems could be proved in the case of III and IV in the presence of donor mols. (THF, pyridine).

IT **24356-03-4**, Dibenzylzirconium dichloride **31247-54-8**, Dibenzyltitanium dibromide **85412-32-4**, Dibenzyltitanium dichloride **108815-99-2**, Dibenzyltitanium diiodide **108816-02-0**, Dibenzylzirconium dibromide **108816-04-2**, Dibenzylzirconium diiodide
(NMR of)

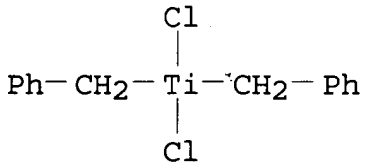
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



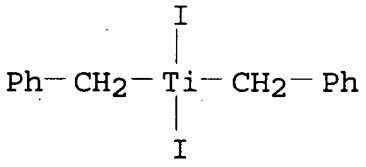
RN 31247-54-8 ZCA
CN Titanium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



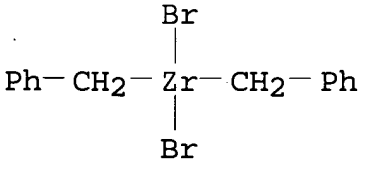
RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



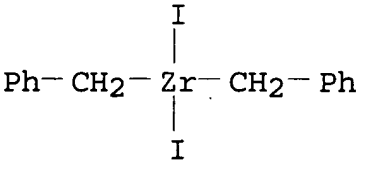
RN 108815-99-2 ZCA
CN Titanium, diiodobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-02-0 ZCA
CN Zirconium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 108816-04-2 ZCA
CN Zirconium, diiodobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



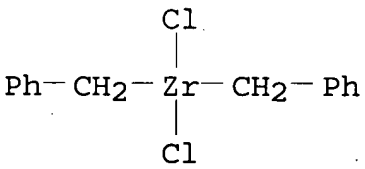
IT **24356-03-4**, Dibenzylzirconium dichloride **31247-54-8**, Dibenzyltitanium dibromide **85412-32-4**, Dibenzyltitanium dichloride **108815-99-2**, Dibenzyltitanium diiodide **108816-02-0**, Dibenzylzirconium dibromide **108816-04-2**, Dibenzylzirconium diiodide
(NMR of)

L18 ANSWER 18 OF 28 ZCA COPYRIGHT 2007 ACS on STN
104:186886 Preparation of polymerization-filled polyethylene in the presence of catalysts based on organic and hydride compounds of titanium, zirconium, and chromium. Semikolenova, N. V.; Nesterov, G. A.; Zakharov, V. A. (Inst. Katal., Novosibirsk, USSR). Vysokomolekulyarnye Soedineniya, Seriya A, 28(1), 166-71 (Russian) **1986.** CODEN: VYSAAF. ISSN: 0507-5475.

AB Org. and tetrahydroborate compds. of Ti, Cr, and Zr supported on natural aluminosilicates were used as catalyst-fillers for the polymn. of ethylene. The catalysts exhibited high activity and did not require addnl. activation with org. Al compds. The most active systems were formed by supporting Zr(BH4)4 and dicyclopentadienylchromium [1271-24-5] on tuff, pumice, and kaolin. The nature of reaction of the complexes with the surface OH groups of the aluminosilicates was similar to that with silica gel. The supported systems had a low content of the transition metal.

IT **24356-03-4**
(catalysts, on natural aluminosilicate supports, for polymn. filling of ethylene)

RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**
(catalysts, on natural aluminosilicate supports, for polymn. filling of ethylene)

L18 ANSWER 19 OF 28 ZCA COPYRIGHT 2007 ACS on STN
101:91488 Reactions of growth limitation of the polymer chain during polymerization of ethylene on supported organometallic catalysts. Zakharov, V. A.; Echevskaya, L. G.; Nesterov, G. A.; Dudchenko, V. K.; Lesnikova, N. P. (Inst. Katal., Novosibirsk, USSR). Vysokomolekulyarnye Soedineniya; Seriya A, 26(5), 993-7 (Russian) **1984.** CODEN: VYSAAF. ISSN: 0507-5475.

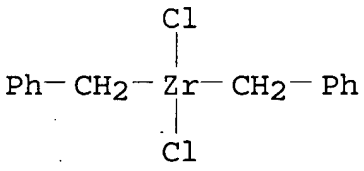
AB In the polymn. of ethylene (I) [74-85-1] in the presence of

supported organometallic catalysts (mainly allyl, benzyl, and BH4 complexes of Zr), chain transfer to I occurred and was, in most cases, the main process limiting chain growth. The ratio of the chain propagation rate const. to the rate consts. of chain transfer to monomer and spontaneous chain transfer was detd. for various catalysts. The role of spontaneous chain transfer increased at low monomer concns. The polyethylene [9002-88-4] obtained contained mainly vinyl groups with insignificant contents of vinylidene and trans-vinylene groups.

IT **24356-03-4**
(catalysts, supported, for polymn. of ethylene, kinetics of chain transfer and propagation in relation to)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**
(catalysts, supported, for polymn. of ethylene, kinetics of chain transfer and propagation in relation to)

L18 ANSWER 20 OF 28 ZCA COPYRIGHT 2007 ACS on STN

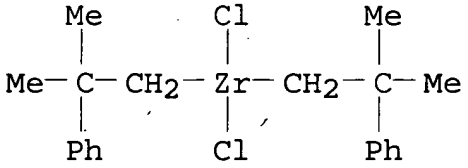
100:175371 Tetraalkyl titanium and zirconium metal chloride catalyst systems for ethylene polymerization. Herskovitz, Thomas (Cent. Res. Dev., E. I. du Pont de Nemours Co., Wilmington, DE, 19898, USA). Journal of Polymer Science, Polymer Chemistry Edition, 22(3), 637-44 (English) **1984.** CODEN: JPLCAT. ISSN: 0449-296X.

AB The C2H4 polymn. activity of (neophyl)nZrCl4-n shows a 20-fold increase from n = 4 to n = 3 and a further 10-fold increase at n = 2. The heterogeneous MR4/TiCl4 catalysts (M = Ti, R = PhCH2; M = Zr, R = PhCH2, neophyl) were developed. To explore the breadth of extendability, other metal chlorides (main group and transition metal) were substituted for TiCl4. Excess AlCl3 or MgCl2 and the MR4 compds. also produced ethylene polymn. catalysts. The inactivity of corresponding (neophyl)4Ti systems is attributed to sterics.

IT **89820-55-3**
(catalysts, for polymn. of ethylene)

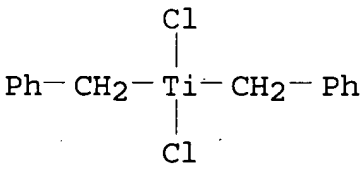
RN 89820-55-3 ZCA

CN Zirconium, dichlorobis(2-methyl-2-phenylpropyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **89820-55-3**
(catalysts, for polymn. of ethylene)

L18 ANSWER 21 OF 28 ZCA COPYRIGHT 2007 ACS on STN
98:179649 Organo(transition metal) compounds. Thiele, Karl Heinz; Schlegel, Michael; Baumann, Hans J. (VEB Leuna-Werke "Walter Ulbricht", Ger. Dem. Rep.). Ger. (East) DD 157559 A1 **19821117**, 9 pp. (German). CODEN: GEXXA8. APPLICATION: DD 1981-228507 19810323.
AB Disproportionation of (PhCH2)4Ti with TiX4 (X = Br, Cl) in various ratios gave 71.7% (PhCH2)3TiBr, (PhCH2)2TiCl2, and 55% PhCH2TiBr3. MeTiBr3.2Et2O and Me2TiCl2.2Et2O were similarly prepd.
IT **85412-32-4P**
(prepn. of)
RN 85412-32-4 ZCA
CN Titanium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **85412-32-4P**
(prepn. of)

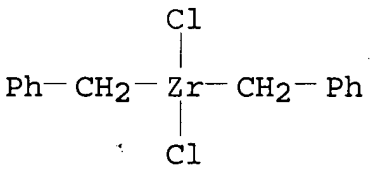
L18 ANSWER 22 OF 28 ZCA COPYRIGHT 2007 ACS on STN
93:150726 Studies of the composition and catalytic properties of supported catalysts prepared through halide-substituted titanium and zirconium benzyl complexes. Nesterov, G. A.; Zakharov, V. A.; Ermakov, Yu. I.; Thiele, K. H.; Schlegel, M.; Drevs, H. (Inst. Catal., Novosibirsk, USSR). Reaction Kinetics and Catalysis Letters, 13(4), 401-6 (English) **1980**. CODEN: RKCLAU. ISSN: 0304-4122.
AB The properties of the title catalysts, prepd. by interaction of Ti(CH2Ph)3X (X = F, Cl, Br) (I) or Zr(CH2Ph)2Cl2 (II) [**24356-03-4**] with silica or alumina, were studied in ethylene polymn. Silica-supported I or II gave polyethylene [9002-88-4] with lower mol. wt. compared with a Zr(CH2Ph)4 [24356-01-2]/SiO2

catalysts. Al2O3-supported Zr(CH2Ph)4 or Ti(CH2Ph)4 was more active than the corresponding Al2O3-supported halide-contg. catalyst. A sharp increase in activity was obsd. for Zr(CH2Ph)2Cl2/SiO2 as compared with Zr(CH2Ph)4/SiO2.

IT **24356-03-4**
(catalysts, for polymn. of ethylene)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**
(catalysts, for polymn. of ethylene)

L18 ANSWER 23 OF 28 ZCA COPYRIGHT 2007 ACS on STN

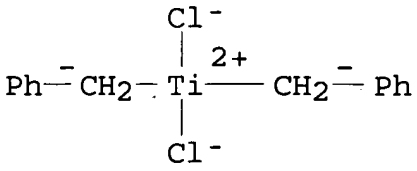
89:180119 Contributions to the chemistry of transition metal alkyl compounds. XXVI. Organotitanium(II) compounds - preparation and properties of dibenzyl- and diphenyltitanium. Thiele, K. H.; Roeder, A.; Moerke, W. (Sekt. Chem., Tech. Hochsch. "Carl Schorlemmer", Merseburg, Ger. Dem. Rep.). Zeitschrift fuer Anorganische und Allgemeine Chemie, 441, 13-22 (German) **1978**. CODEN: ZAACAB. ISSN: 0044-2313.

AB (PhCH2)2Ti (22%) and Ph2Ti (30%) were prepd. by reactions of (C5H5)2Ti(CH2Ph)2 and (C5H5)2TiPh2 with PhCH2Li and PhLi. (PhCH2)2Ti was also prepd. by disproportionation of (PhCH2)3Ti. (PhCH2)2Ti forms definite coordination compds. with 1,4-dioxane, 2,2'-bipyridine, and MgCl2 and a clathrate (PhCH2)2Ti.MgCl2.C6H6.

IT **68080-16-0P 68080-17-1P**
(prepn. of)

RN 68080-16-0 ZCA

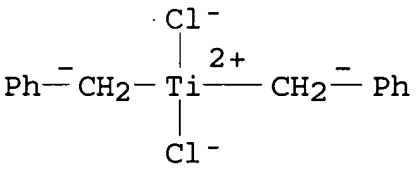
CN Titanate(2-), dichlorobis(phenylmethyl)-, magnesium (1:1), (T-4)- (9CI) (CA INDEX NAME)



RN 68080-17-1 ZCA
CN Titanate(2-), dichlorobis(phenylmethyl)-, (T-4)-, magnesium, compd. with benzene (1:1:1) (9CI) (CA INDEX NAME)

CM 1

CRN 68080-16-0
CMF C14 H14 Cl2 Ti . Mg
CCI CCS



CM 2

CRN 71-43-2
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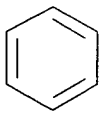


IT **68080-16-0P 68080-17-1P**

(prepn. of)

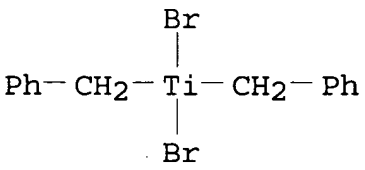
L18 ANSWER 24 OF 28 ZCA COPYRIGHT 2007 ACS on STN
86:74052 Stereospecificity of the action of benzyl derivatives of titanium(IV) during polymerization of isoprene and the nature of the active center. Vydrina, T. K.; Guzman, I. Sh.; Dolgoplosk, B. A.; Tinyakova, E. I.; Sharaev, O. K.; Yakovleva, O. N. (Inst. Neftekhim. Sint. im. Topchieva, Moscow, USSR). Doklady Akademii Nauk SSSR, 230(3), 602-4 (Russian) **1976.** CODEN: DANKAS. ISSN: 0002-3264.

AB The polymn. of isoprene [78-79-5] in the presence of benzyl derivs. of Ti of the type (PhCH2)nTiX4-n (where n = 2-4 and X = Cl, Br, or I) in PhMe or o-xylene showed that (PhCH2)4Ti [17520-19-3] led to the formation of polyisoprene (I) contg. primarily 1,4-trans segments, whereas (PhCH2)3TiX altered the stereospecificity toward increasing content of 1,4-cis and 3,4-segments. Similar changes in stereospecificity were obsd. during the catalytic polymn. of butadiene [106-99-0]. Electron-donor solvating additives e.g., Ph3P [603-35-0] or THF [109-99-9] altered the stereospecifity of (PhCH2)3TiI [31247-52-6] towards the formation of 3,4-segments in I and 1,2-segment in polybutadiene. The EPR spectra suggested that in the active center Ti remained in the tetravalent state.

IT **31247-54-8**
(catalysts, for polymn. of dienes, polymer stereospecificity in relation to)

RN 31247-54-8 ZCA

CN Titanium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **31247-54-8**
(catalysts, for polymn. of dienes, polymer stereospecificity in relation to)

L18 ANSWER 25 OF 28 ZCA COPYRIGHT 2007 ACS on STN
75:6669 Tetrabenzylzirconium, -titanium, and -hafium complexes as polymerization initiators. Pioli, Alexander J. P.; Hollyhead, William B.; Todd, Peter F. (Imperial Chemical Industries Ltd.). Ger. Offen. DE 2026032 **19710318**, 27 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1970-2026032 19700527.

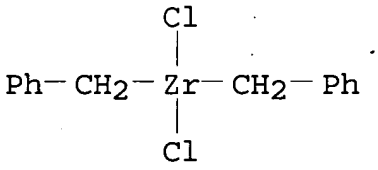
GI For diagram(s), see printed CA Issue.

AB Tetrabenzylhafnium, Ti, and Zr complexes [I, M = Ti, Zr or Hf, R = H, OMe, Me, F or Cl; R1 = H and R2 = H, Cl or Me, or (R1R2) =

CH:CHCH:CH, R3 = H or Me] were prepd. and used to initiate polymn. of ethylene, p-BrC6H4CH:CH2, or propylene. Thus, ZrCl4 treated 2 hr with PhCH2MgCl in Et2O at -20° gave I (M = Zr, R = R1 = R2 = R3 = H) (II). Polymn. of ethylene in PhMe in the presence of II rather than conventional (PhCH2)4Ti, gave increased polyethylene yields. Nineteen other I were similarly prepd. and used; (PhCH2)3ZrCl and (PhCH2)2ZrCl2 were also prepd.

IT **24356-03-4**
(catalysts, for polymn. of olefins)

RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



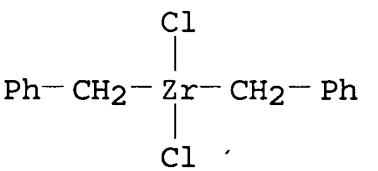
IT **24356-03-4**
(catalysts, for polymn. of olefins)

L18 ANSWER 26 OF 28 ZCA COPYRIGHT 2007 ACS on STN
74:112161 Synthesis and properties of some titanium and zirconium benzyl derivatives. Zucchini, U.; Albizzati, E.; Giannini, Umberto (Cent. Ric., Montecatini Edison S.p.A., Milan, Italy). Journal of Organometallic Chemistry, 26(3), 357-72 (English) **1971.** CODEN: JORCAI. ISSN: 0022-328X.

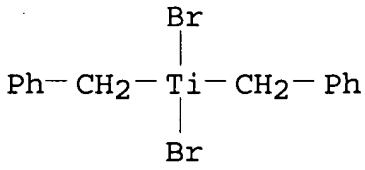
AB Syntheses of Ti(CH2Ph)4 (I), Zr(CH2Ph)4 (II) and their halogen and alkoxy derivs. are described. Their phys. properties and reactivity with H, O, CO2 and olefins was investigated. Spectroscopic and chem. data are consistent with the σ-nature of the metal-C bond. I and II react in a different way with Al(CH2Ph)3 to form polynuclear complexes.

IT **24356-03-4P 31247-54-8P**
(prepn. of)

RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



RN 31247-54-8 ZCA
CN Titanium, dibromobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)

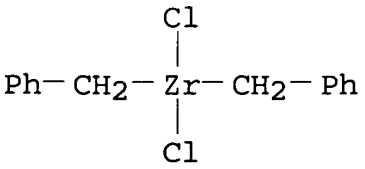


IT **24356-03-4P 31247-54-8P**
(prepn. of)

L18 ANSWER 27 OF 28 ZCA COPYRIGHT 2007 ACS on STN
73:110174 Polymerization of olefins with benzyl derivatives of titanium and of zirconium. Giannini, Umberto; Zucchini, U.; Albizzati, E. (Centro Ric. Milano, Montecatini Edison S.p.A., Milan, Italy). Journal of Polymer Science, Polymer Letters Edition, 8(6), 405-10 (English) **1970.** CODEN: JPYBAN. ISSN: 0360-6384.

AB The possibility of prepg. isotactic polyolefins by using sol. catalysts and the nature of the active centers in, e.g. (PhCH2)4Ti, (PhCH2)3TiCl, (PhCH2)4Zn, (PhCH2)3ZnCl, (PhCH2)2ZnCl2, and (PhCH2)3TiF, and similar compds. were investigated. In the polymn. of C2H4, the catalytic activity of the halogenated derivs. was greater than that of the corresponding tetrabenzyl derivs. and increased with increasing no. of halogen atoms. Some of the halogen-free organometallic transition metal compds. stereospecifically polymd. α-olefins in the absence of organoaluminum compds., but the presence of organoaluminum compds. increased the catalytic activity of all of the benzyl-transition metal compds. studied. A metallation reaction of the methylenic group of (C6H5CH2)4Ti by Al was indicated.

IT **24356-03-4**
(catalysts, for polymn. of olefins)
RN 24356-03-4 ZCA
CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4**
(catalysts, for polymn. of olefins)

L18 ANSWER 28 OF 28 ZCA COPYRIGHT 2007 ACS on STN
72:12845 Benzylzirconium compounds. Zucchini, U.; Giannini, U.; Albizzati, E.; D'Angelo, R. (Centro Ric., Montecatini Edison S.p.A.,

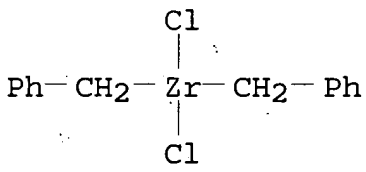
Milan, Italy). Journal of the Chemical Society [Section] D: Chemical Communications (20), 1174-5 (English) **1969.** CODEN: CCJDAO. ISSN: 0577-6171.

AB ClMgCH2Ph and ZrCl4 in Et2O at -15° give Zr(CH2Ph)4 (I), m. 133-4°. I slowly decomps. in hydrocarbon soln. at 110° to give PhMe and low-valency Zr compds. I and H at 50° and atm. pressure give PhMe. Redn. products of I behave as hydrogenation catalysts for aromatic rings at 50°. I reacts with 1 or 2 moles of HCl gas in aromatic solvents to give PhMe and (PhCH2)3ZrCl, m. 89°, or (PhCH2)2ZrCl2 (decompd. >100°), resp. All benzyl derivs. of Zr show catalytic activity in the polymn. of C2H4 and α-olefins.

IT **24356-03-4P**
(prepn. of)

RN 24356-03-4 ZCA

CN Zirconium, dichlorobis(phenylmethyl)-, (T-4)- (9CI) (CA INDEX NAME)



IT **24356-03-4P**
(prepn. of)

Access DB# [redacted] 215057

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: LEE, RICHARD A. Examiner #: 78680 Date: 02-07-2007
Art Unit: 1713 Phone Number 11CA Serial Number: 10/500,543
Mail Box and Bldg/Room Location: REM 10A 21 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

****

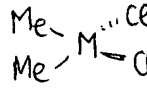
Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: PREPARATION OF DIALKYL-ANSA-METALLOCENES

Inventors (please provide full names): SCHOTTEK, J.
SCHAUER, D.

Earliest Priority Filing Date: JAN-08-2002

**For Sequence Searches Only* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.*

Please search for use of  in preparation of metallocenes†

M= Ti, Zr, Hf

sample nomenclature:

dichlorodimethylzirconium
dichloro-zirconium dimethyl
dimethylzirconium dichloride

and permutations thereof

† any metallocene/metallocene-like complex, ie. Cp, Indenyl, Fluorenyl

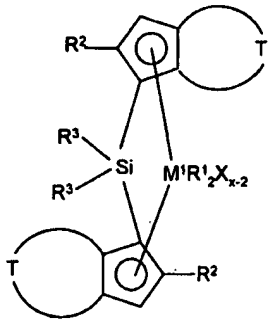
****

STAFF USE ONLY	Type of Search	Vendors and cost where applicable
Searcher: EJ	NA Sequence (#)	STN
Searcher Phone #:	AA Sequence (#)	Dialog
Searcher Location:	Structure (#)	Questel/Orbit
Date Searcher Picked Up:	Bibliographic	Dr.Link
Date Completed: 2-9-07	Litigation	Lexis/Nexis
Searcher Prep & Review Time:	Fulltext	Sequence Systems
Clerical Prep Time:	Patent Family	WWW/Internet
Online Time:	Other	Other (specify)

PTO-1590 (8-01)

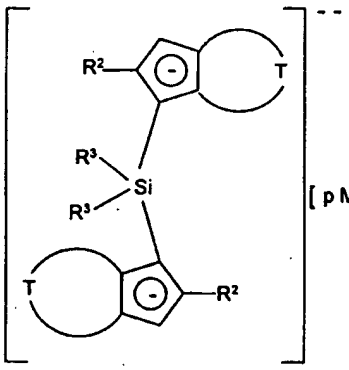
AMENDMENTS TO THE CLAIMS

1. (currently amended) A process for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I)



(I)

which comprises reacting a ligand starting compound of the formula (II)



(II)

with a transition metal dialkyl compound of the formula (III)

$$M^1X_xR^1{}_2{}^*D_y \quad \text{(III)},$$

where

M^1 is an element of group 4, 5 or 6 of the Periodic Table of the Elements[[,]];

R^1 are identical C_1-C_{20}-alkyl or C_7-C_{40}-arylalkyl radicals[[,]];

X are identical or different halogens[[,]];

R^2 are identical or different C_1-C_{40} radicals[[,]];

R^3 are identical or different C_1-C_{40} radicals[[,]];

T is a divalent C_1-C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12 atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring[[,]];

M^2 is Li, Na, K, MgCl, MgBr, MgI, Mg or Ca[[,]];

D is an uncharged Lewis base ligand[[,]];

x is equal to the oxidation number of M^1 minus 2[[,]];

y is from 0 to 2;

and

p is 1 in the case of doubly positively charged metal ions or 2 in the case of singly positively charged metal ions or metal ion fragments.

2. (currently amended) ~~A~~The process as claimed in claim 1, wherein

T is a 1,3-butadiene-1,4-diyl group which may be unsubstituted or be substituted by from 1 to 4 radicals R^4, where the two 1,3-butadiene-1,4-diyl groups may be different[[,]];

R^4 are identical or different C_1-C_{20} radicals[[,]];

M^1 is titanium, zirconium or hafnium[[,]];

R^1 are identical C_1-C_5-alkyl or C_7-C_{20}-arylalkyl radicals[[,]]; and

X is halogen ~~and~~

~~R^2, R^3, M^2, D, p, x and y are as defined in claim 1~~.

3. (currently amended) ~~A~~The process as claimed in claim 1 ~~or 2~~, wherein the transition metal dialkyl compound of the formula (III) is produced at above –30°C by combining a compound M^1X_{x+2} with from 2 to 2.5 equivalents of a compound R^1M^3 in the presence of a ligand compound D, where

M^3 is Li^+, Na^+, K^+, $MgCl^+$, $MgBr^+$, MgI^+, ½ $[Mg^{++}]$ or ½ $[Zn^{++}]$, ~~and~~

~~the other variables are as defined in claim 1 or 2~~.

4. (currently amended) ~~A~~The process as claimed in claim 1 ~~or 2~~, wherein the ligand starting compound of the formula (II) ~~or (V)~~ is combined with the transition metal dialkyl compound of the formula (III) at above –30°C.

5. (currently amended) ~~A~~The process as claimed in claim 4, wherein ~~the~~a reaction mixture is maintained at from 30°C to 150°C for a period of at least 10 minutes after the reaction components have been combined.

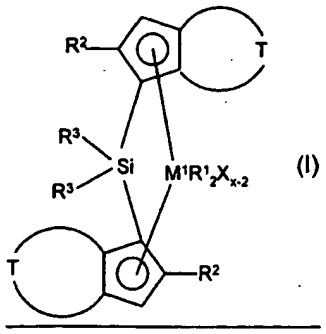
6. (currently amended) ~~A~~The process as claimed in ~~any of claims~~claim 1 ~~to 5~~, wherein the reaction is carried out in an organic solvent or solvent mixture which comprises at least 10% by volume of an ether.

7. (currently amended) ~~A~~The process as claimed in ~~any of claims~~claim 1 ~~to 6~~, wherein ~~the~~a racemoselectivity = (proportion of rac – proportion of meso)/(proportion of rac + proportion of meso) is greater than zero.

8. (currently amended) ~~The use of~~A process comprising utilizing a transition metal dialkyl compound of the formula (III):

$$M^1X_xR^1{}_2{}^*D_y \quad \text{(III)}$$

for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I):



(I)

wherein

M^1 is an element of group 4, 5 or 6 of the Periodic Table of the Elements;

R^1 are identical C_1-C_{20}-alkyl or C_7-C_{40}-arylalkyl radicals;

X are identical or different halogens;

R^2 are identical or different C_1-C_{40} radicals;

R^3 are identical or different C_1-C_{40} radicals;

D is an uncharged Lewis base ligand;

y is from 0 to 2;

T is a divalent C_1-C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12 atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring; and

x is equal to the oxidation number of M^1 minus 2.

9. (new) The process as claimed in claim 2, wherein the transition metal dialkyl compound of the formula (III) is produced at above –30°C by combining a compound M^1X_{x+2} with from 2 to 2.5 equivalents of a compound R^1M^3 in the presence of a ligand compound D, where

M^3 is Li^+, Na^+, K^+, $MgCl^+$, $MgBr^+$, MgI^+, ½ [Mg^{++}] or ½ [Zn^{++}].

10. (new) The process as claimed in claim 2, wherein the ligand starting compound of the formula (II) is combined with the transition metal dialkyl compound of the formula (III) at above –30°C.

11. (new) The process as claimed in claim 10, wherein a reaction mixture is maintained at from 30°C to 150°C for a period of at least 10 minutes after the reaction components have been combined.

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Bib Data Sheet

CONFIRMATION NO. 6726

SERIAL NUMBER	FILING OR 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
10/500,543	12/20/2004 RULE	525	1712	LU 6001 (US)

APPLICANTS

Jorg Schottek, Frankfurt, GERMANY;
Diana Schauer, Bruchkobel, GERMANY;

**** CONTINUING DATA ***************************

This application is a 371 of PCT/EP02/14379 12/17/2002

**** FOREIGN APPLICATIONS *********************

GERMANY 102 00 422.6 01/08/2002

Foreign Priority claimed	STATE OR COUNTRY	SHEETS DRAWING	TOTAL CLAIMS	INDEPENDENT CLAIMS
☐ yes ☐ no 35 USC 119 (a-d) conditions met ☐ yes ☐ no ☐ Met after Allowance Verified and Acknowledged Examiner's Signature Initials	GERMANY		11	2

ADDRESS

34872

TITLE

Preparation of dialkyl-ansa-metallocenes

FILING FEE RECEIVED	FEES: Authority has been given in Paper No. _____ to charge/credit DEPOSIT ACCOUNT No. _____ for following:
1050	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

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L6           10 S L5 AND RSD/FA
L7           28 S L5 NOT L6

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L9           19 S L7

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L14           6 S L11 AND L13
L15          36 S L12 NOT L14
L16           4 S L12 AND L14
L17           6 S L14 OR L16
L18          28 S 1840-2002/PY,PRY AND L10
L19         105 S 1840-2002/PY,PRY AND L11
L20           6 S L17 AND L19
L21          27 S L15 AND L19

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L22          46 S ?METALLOCEN? OR ?METALOCEN?
L23           0 S L9 AND L22
L24          91 S L11 NOT (L20 OR L21)
L25          72 S L24 AND L19
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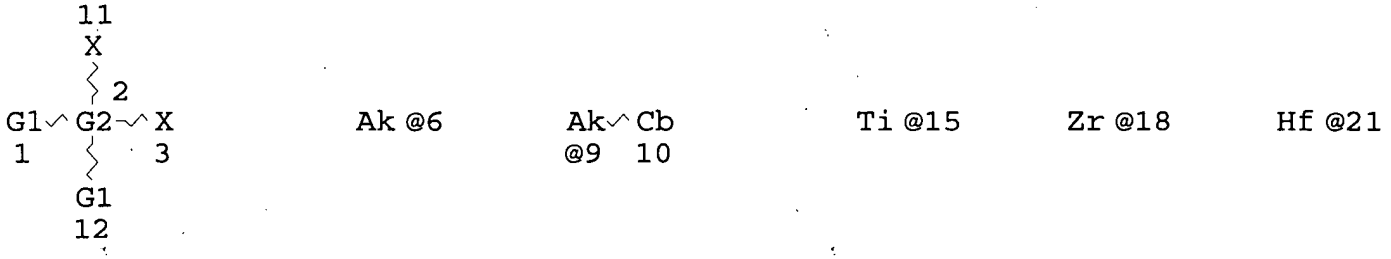

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STEREO ATTRIBUTES: NONE
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FILE LAST UPDATED: 01 May 1997 (19970501/UP)

=> D L9 1-19 TI

L9 ANSWER 1 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI mechanism of N fixation in the (C5H5)2 TiCl2-C2H5MgBr system

L9 ANSWER 2 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI process for purifying liquids or dissolved compds. of halides, halide hydrides, alkyls, and alkoxyls

L9 ANSWER 3 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI kinetics of the polymerization of styrene-α-d and(or) styrene by homogeneous catalysis - (II)

L9 ANSWER 4 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polymerization of deuterioethylene on the homogeneous catalytic system Et2TiCl2 + Me2AlCl

L9 ANSWER 5 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI double-bond opening and isomerization and H-exchange reactions in the polymerization of dideuterioethylene

L9 ANSWER 6 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI carbon (diamond-structured), low-pressure prepn. of

L9 ANSWER 7 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI Raman and infrared spectra of selenous acid and pyroselenites
TI infrared spectra of trimethyl Al, dimethyl AlCl3, methyl Al2Cl2, methyl TiCl3 dimethyl TiCl2, and some D derivs.

L9 ANSWER 8 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI region of the ternary system BaO-SrO-Fe2O3 - (I) equil. diagram of the 1100° isotherm of the region lying between Fe2O3, 2BaO.Fe2O3, and 2SrO.Fe2O3

L9 ANSWER 9 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI dimethyltitanium dichloride

L9 ANSWER 10 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polymerization of C2H4 with alkyltitanium halide catalysts
TI polymerization of ethylene with alkyltitanium halide catalysts

L9 ANSWER 11 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI allylmanganese tetracarbonyls

L9 ANSWER 12 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI purification of unsatd. aldehydes

L9 ANSWER 13 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polystyrene polymerization catalyzed by organotitanium compds.

L9 ANSWER 14 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polymerization of propylene, butadiene, isoprene, and chloroprene

L9 ANSWER 15 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI catalysis of the isocyanate-hydroxyl reaction

L9 ANSWER 16 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polystyrene
TI reinforced polymers

L9 ANSWER 17 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polymerization of propylene, butadiene, isoprene, and chloroprene

L9 ANSWER 18 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI polystyrene

L9 ANSWER 19 OF 19 CAOLD COPYRIGHT 2007 ACS on STN
TI nonaq. morpholine

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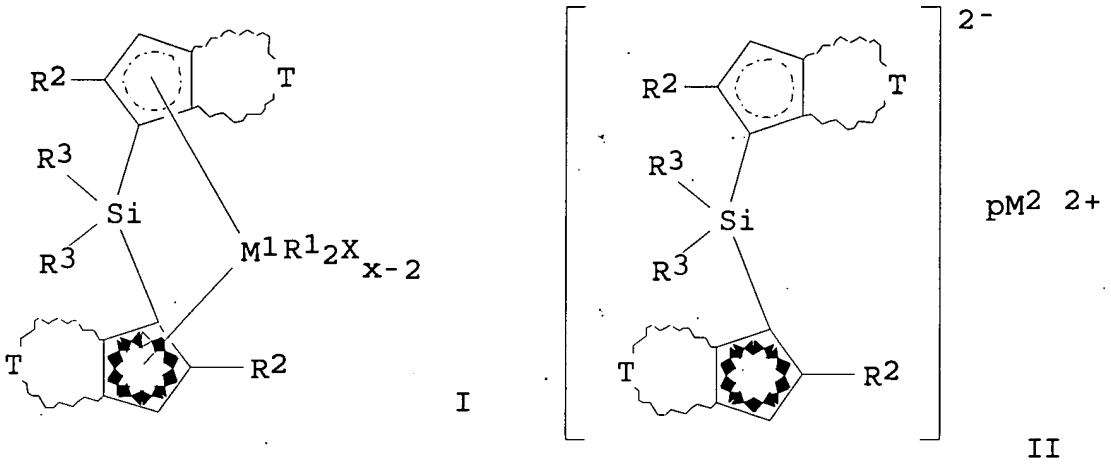
L20 ANSWER 1 OF 6 ZCA COPYRIGHT 2007 ACS on STN
139:101272 Racemoselective process for the preparation of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compounds. Schottek, Joerg; Schauer, Diana (Basell Polyolefine G.m.b.H., Germany). PCT Int. Appl. WO 2003057704 A1 20030717, 16 pp. DESIGNATED STATES: W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ,

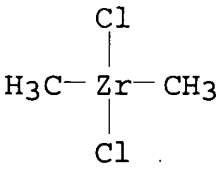
OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2002-EP14379 20021217. PRIORITY: DE 2002-10200422 20020108.

GI



AB Silicon-bridged dialkyl-ansa-**metallocenes** [I; M1 = Group 4, 5 or 6 element; R1 = C1-C20 alkyl or C7-C40 arylalkyl; X = halogen, R2, R3 = C1-C40 radicals; T = divalent C1-C40 group which together with the cyclopentadienyl ring forms a further (un)satd. ring system which has a ring size of 5-12 atoms, where T may contain Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring; M2 = Li, Na, K, MgCl, MgBr, MgI, Mg, Ca; D = uncharged Lewis base ligand; x = oxidn. no. of M1 minus 2, y = 0-2; p = 1 in the case of doubly pos. charged metal ions or 2 in the case of singly pos. charged metal ions or metal ion fragments], useful in catalyst systems for olefin polymn. (no data), are prepd. by reaction of a ligand (II; same R2, R3, T, M2, p) with a transition metal dialkyl compd. M1XxR12*Dy (same M1, X, R1, D, x, y), preferably in an org. solvent or solvent mixt. contg. ≥10% by vol. of an ether, where the reactants are combined at >-30° and then the reaction mixt. is maintained at 30-150° for ≥10 min. In the example given, treating 10 g (21.3 mmol) dimethylbis(2-methyl-4-phenyl-1-indenyl)silane in 236 mL THF with 2.2 equiv BuLi in PhMe at 0°, followed by treatment with 21.3 mmol Me2ZrCl2 in THF at 0° and subsequent heating at 65° for 4.5 h gave 31% of the rac isomer of Me2Si(Cpind)2ZrMe2 (Cpind = 2-methyl-4-phenyl-1-indenyl).

IT **192726-11-7**, Dimethylzirconium dichloride
(racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
RN 192726-11-7 ZCA
CN Zirconium, dichlorodimethyl-, (T-4)- (9CI) (CA INDEX NAME)



IC ICM C07F017-00
ICS C07F007-08; C07F007-00
CC 29-11 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 35
ST **metallocene** ansa silicon bridged dialkyl prepn
IT **Metallocenes**
(ansa-; racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
IT Group IVB element compounds
Group VB element compounds
Group VIB element compounds
(racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
IT Stereoselective synthesis
(racemoselective; racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
IT **192726-11-7**, Dimethylzirconium dichloride
(racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
IT 153733-76-7
(racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)
IT 154827-36-8P
(racemoselective prepn. of silicon-bridged dialkyl-ansa-**metallocenes** by reaction of bridged ligand with Group 4, 5 or 6 metal dialkyl compds.)

L20 ANSWER 2 OF 6 ZCA COPYRIGHT 2007 ACS on STN
135:358008 Metalations with Group 4 Alkylmetal(IV) Halides: Expeditious

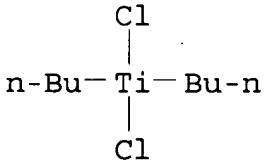
Route to **Metallocene** and **Nonmetallocene** Procatalysts. Eisch, John J.; Owuor, Fredrick A.; Otieno, Peter O. (Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY, 13902-6016, USA). Organometallics, 20(20), 4132-4134 (English) **2001.** CODEN: ORGND7. ISSN: 0276-7333. OTHER SOURCES: CASREACT 135:358008. Publisher: American Chemical Society.

AB Group 4 (IVB) alkylmetal(IV) halides Bu2MtCl2 (Mt = Ti, Zr, Hf), generated in hydrocarbon media at -78° by treating MtCl4 with 2 equiv of BuLi, function as strong bases toward a variety of Bronsted acids, EH, where E = cyclopentadienyl or substituted cyclopentadienyl, 1-alkynyl, indenyl, alkoxy, aryloxy, and disubstituted amino, to form **metallocene** and **nonmetallocene** olefin polymn. procatalysts, E2MCl2, expeditiously and generally in high yield. E.g., Bu2ZrCl2, formed in situ from BuLi and ZrCl4 in hexane or toluene under Ar at -78°, reacted with CpH (cyclopentadiene) to give pure Zirconocene dichloride in 95% yield.

IT **23307-60-0P**, Dibutyldichlorotitanium **223594-30-7P**, Dibutyldichlorozirconium **372201-02-0P**, Dibutyldichlorohafnium
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

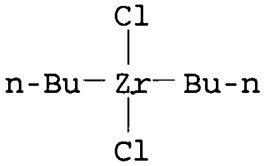
RN 23307-60-0 ZCA

CN Titanium, dibutyldichloro-, (T-4)- (9CI) (CA INDEX NAME)



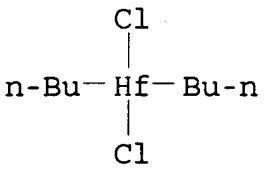
RN 223594-30-7 ZCA

CN Zirconium, dibutyldichloro-, (T-4)- (9CI) (CA INDEX NAME)



RN 372201-02-0 ZCA

CN Hafnium, dibutyldichloro-, (T-4)- (9CI) (CA INDEX NAME)



CC 29-10 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 35, 67

ST metalation Bronsted acid Group IVB alkylmetal halide; **metallocene** procatalyst prepn; **nonmetallocene** procatalyst prepn; cyclopentadiene metalation Group IVB alkylmetal halide; alkyne metalation Group IVB alkylmetal halide; indene metalation Group IVB alkylmetal halide; alc metalation Group IVB alkylmetal halide; aryl alc metalation Group IVB alkylmetal; alkanol metalation Group IVB alkylmetal; titanium alkyl halide metalation Bronsted acid; zirconium alkyl halide metalation Bronsted acid; hafnium alkyl halide metalation Bronsted acid; procatalyst **metallocene nonmetallocene** prepn Group IVB alkyl halide metalation; catalyst **metallocene nonmetallocene** prepn Group IVB alkyl halide metalation; ansa **metallocene** dichloride prepn; constrained geometry contg Group IVB metal procatalyst prepn; olefin polymn procatalyst Group IVB **metallocene nonmetallocene** prepn; amino disubstituted metalation Group IVB alkylmetal halide

IT **Metallocenes**
(Group IVB metal; metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Transition metal halides
(Group IVB; metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Alcohols, preparation
(complexes; metalations of alcs. with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Alkynes
(complexes; metalations of alkynes with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Phenols, preparation
(complexes; metalations of phenols with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Group IVB element compounds
(halides; metalations of Bronsted acids with Group 4 (IVB)

alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Bronsted acids
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT Group IVB element complexes
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts for olefin polymn. catalysts)

IT Polyolefins
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts for olefin polymn. catalysts)

IT Polymerization catalysts
(olefin; metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts for)

IT Amines, preparation
(secondary, complexes; metalations of disubstituted amines with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT 1271-19-8P, Titanocene dichloride 1291-32-3P, Zirconocene dichloride 12113-02-9P, Dichlorobis(η5-indenyl)titanium 12116-66-4P, Hafnocene dichloride 12148-49-1P, Dichlorobis(η5-indenyl)zirconium 49596-05-6P, Dichlorobis(η5-indenyl)hafnium 71297-23-9P 372201-03-1P 372201-05-3P
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT 67-63-0, Isopropanol, reactions 95-13-6, Indene 109-72-8, Butyllithium, reactions 536-74-3, Phenylacetylene 542-92-7, Cyclopentadiene, reactions 579-43-1, meso-Hydrobenzoin 7550-45-0, Titanium tetrachloride, reactions 10026-11-6, Zirconium tetrachloride 13499-05-3, Hafnium tetrachloride 129149-21-9
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

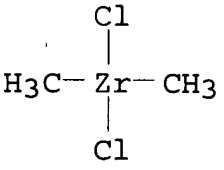
IT 762-99-2P, Dichlorobis(isopropanolato)titanium **23307-60-0P**, Dibutyldichlorotitanium **223594-30-7P**, Dibutyldichlorozirconium **372201-02-0P**, Dibutyldichlorohafnium 372201-04-2P, Dibutylbis(isopropanolato)titanium
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

IT 350230-64-7P, Titanium(II) isopropoxide
(metalations of Bronsted acids with Group 4 (IVB) alkylmetal(IV) halides as expeditious route to **metallocene** and **nonmetallocene** procatalysts)

L20 ANSWER 3 OF 6 ZCA COPYRIGHT 2007 ACS on STN
131:337531 **Metallocene** compound having heteroatomic bridge and method for producing polymer by using it as polymerization catalyst. Huh, Wan-Soo; Lee, Dong-Ho; Noh, Seok-Kyun (Korea Academy of Industrial Technology, S. Korea). U.S. US 5986025 A **19991116**, 6 pp., Cont. of U.S. Ser. No. 540,966, abandoned. (English). CODEN: USXXAM. APPLICATION: US 1997-852040 19970506. PRIORITY: KR 1994-26500 19941013; US 1995-540966 19951011.

AB Title compd., including a neutral **metallocene**, a cationic **metallocene**, and a supported **metallocene**, is useful for polymg. α-olefin, cycloolefin, and/or diene in the presence of an organometallic cocatalyst. Thus, ethylene and propylene were polymd. using a **metallocene** compd. having heteroat. bridge such as tetra-Me disiloxanebis(η5-cyclopentadienyl)zirconium dichloride (prepn. given) and Me aluminoxane to give a polymer with m.p. 117°, crystn. temp. 103°, and catalyst activity 20.1 kg polymer/g Zr-atm-h.

IT **192726-11-7P**, Dimethylzirconium dichloride
(reactant; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
RN 192726-11-7 ZCA
CN Zirconium, dichlorodimethyl-, (T-4)- (9CI) (CA INDEX NAME)



IC ICM C08F004-64
ICS C07F017-00
INCL 526119000
CC 35-3 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 29, 67
ST **metallocene** polymn catalyst polyolefin; ethylene propylene copolymer prepn disiloxane cyclopentadienyl zirconium chloride catalyst; methyl aluminoxane cocatalyst polyolefin prepn
IT Aluminoxanes
(Me, cocatalysts; prepn. of polyolefin in presence of polymn. catalyst of **metallocene** compd. having heteroat. bridge)
IT Zeolites (synthetic), uses
(catalyst supports; prepn. of polyolefin in presence of polymn.

catalyst of **metallocene** compd. having heteroat. bridge)
IT Aluminoxanes
(cocatalysts; prepn. of polyolefin in presence of polymn. catalyst of **metallocene** compd. having heteroat. bridge)
IT Polymerization catalysts
(**metallocene**; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT **Metallocenes**
(prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT Polyolefins
(prepn. of polyolefin in presence of polymn. catalyst of **metallocene** compd. having heteroat. bridge)
IT 1344-28-1, Aluminum oxide (Al2O3), uses 7631-86-9, Silica, uses 7784-30-7, Aluminum phosphate 7786-30-3, Magnesium chloride, uses
(catalyst support; prepn. of polyolefin in presence of polymn. catalyst of **metallocene** compd. having heteroat. bridge)
IT 139354-29-3P
(intermediate or catalyst; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT 18402-76-1P
(intermediate; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT 178447-47-7P
(prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT 9002-88-4P, Polyethylene 9010-79-1P, Ethylene-propylene copolymer
(prepn. of polyolefin in presence of polymn. catalyst of **metallocene** compd. having heteroat. bridge)
IT **192726-11-7P**, Dimethylzirconium dichloride
(reactant; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT 917-54-4, Methyl lithium 10026-11-6, Zirconium chloride (ZrCl4)
(reactant; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)
IT 2401-73-2, 1,3-Dichlorotetramethyldisiloxane 4984-82-1, Sodium cyclopentadienylide
(starting material; prepn. of **metallocene** compd. having heteroat. bridge for olefin polymn. catalyst)

L20 ANSWER 4 OF 6 ZCA COPYRIGHT 2007 ACS on STN
131:88219 Polymerization of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis. Matkovskii, P. E.; Russiyan, L. N.; Makhaev, V. D.; Lee, Ahn Ki; Song, Bo Geun (Institute of Problems in Chemical Physics, Russian Academy of Sciences, Moscow, 142432, Russia). Vysokomolekulyarnye Soedineniya, Seriya A i Seriya B, 40(9), 1413-1420 (Russian) **1998**. CODEN: VSSBEE. ISSN:

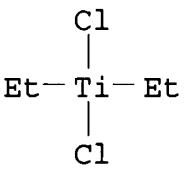
1023-3091. Publisher: MAIK Nauka.

AB The effects of the concn. of the components of the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system, Al:Ti molar ratio, the solvent nature, as well as temp. on the rate of ethylene polymn. and the yield and mol. mass of the resulting polymer were studied. When polymn. was carried out in Et chloride at low concns. of the catalyst, the activity and specific productivity of the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system increased sharply. At [(C5H5)2TiCl2] > 104 mol/L and the Al:Ti molar ratios 1000-2000, the specific productivity of the given catalytic system approached the productivity of the classical **metallocene** catalysts. It was established that the enhanced activity of this system-in Et chloride at 20-40° is assocd. with an increase in the rate const. of chain propagation from 3-10 (toluene) to 360-550 L/(mol s) (Et chloride). It was inferred that the high activity of the **metallocene** catalyst under investigation, which exceeds 30 PE macromolesd/mol (C5H5)2TiCl2, is related to a chain transfer to (C5H5)2AlCl. It was found that, in the temp. range 20-40°, the rate const. of this reaction varies from 0.7 to 6.0 mol/(L s).

IT **2247-00-9**, Diethyltitanium dichloride
(polymn. of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis)

RN 2247-00-9 ZCA

CN Titanium, dichlorodiethyl-, (T-4)- (9CI) (CA INDEX NAME)



CC 35-2 (Chemistry of Synthetic High Polymers)

IT Solvent effect
(on polymn. of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis)

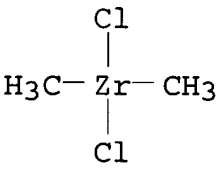
IT Polymerization catalysts
(polymn. of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis)

IT 96-10-6, Diethylaluminum chloride, uses **2247-00-9**, Diethyltitanium dichloride
(polymn. of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis)

IT 9002-88-4P, Polyethylene

(polymn. of ethylene with the (C5H5)2TiCl2-(C2H5)2AlCl catalytic system under the conditions of classical **metallocene** catalysis)

L20 ANSWER 5 OF 6 ZCA COPYRIGHT 2007 ACS on STN
127:121806 An efficient synthetic method of ansa-zirconocene dimethyl complexes via Me2ZrCl2. Park, Joon T.; Woo, Byung Won; Yoon, Sung Cheol; Shim, Sang Chul (Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, 305-701, S. Korea). Journal of Organometallic Chemistry, 535(1-2), 29-32 (English) **1997.** CODEN: JORCAI. ISSN: 0022-328X. OTHER SOURCES: CASREACT 127:121806. Publisher: Elsevier.
AB The reaction of ZrCl4 with 2 equiv. of MeLi to form Me2ZrCl2 followed by in situ metalation of Me2ZrCl2 with the corresponding ansa-ligands produces the resp. ansa-dimethylzirconocene complexes, o-Xyl(Ind)2ZrMe2 [1b, Ind = η5-1-indenyl, o-Xyl = C6H4(CH2)2-1,2], 2-Bu(Ind)2ZrMe2 [2b, 2-Bu = (-CH2CH:CHCH2-)], Et(Ind)2ZrMe2 [3b, Et = (CH2)2] and Me2Si(Ind)2ZrMe2 in high yields. Treatment of 1b-3b with HCl affords ansa-dichlorozirconocene complexes in quant. yields. Synthesis of ansa-dimethylzirconocene via Me2ZrCl2 is more efficient than that via Cp2ZrCl2 (Cp2 = ansa-ligand) in the conventional methods.
IT **192726-11-7P**, Dimethylzirconium dichloride
(prepn. of ansa-zirconocene di-Me complexes via dimethylzirconium dichloride)
RN 192726-11-7 ZCA
CN Zirconium, dichlorodimethyl-, (T-4)- (9CI) (CA INDEX NAME)



CC 29-10 (Organometallic and Organometalloidal Compounds)
IT **Metallocenes**
(ansa-; prepn. of ansa-zirconocene di-Me complexes via dimethylzirconium dichloride)
IT 186413-70-7P **192726-11-7P**, Dimethylzirconium dichloride
(prepn. of ansa-zirconocene di-Me complexes via dimethylzirconium dichloride)

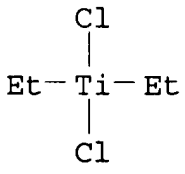
L20 ANSWER 6 OF 6 ZCA COPYRIGHT 2007 ACS on STN
101:131166 Metal-containing initiator systems. 34. Polymerization of vinyl monomers initiated by the binary system cobaltocene/bis(ethyl acetoacetato)copper(II). Mun, Yang Un; Sato, Tsuneyuki; Otsu, Takayuki (Fac. Eng., Osaka City Univ., Osaka, 558, Japan).

Makromolekulare Chemie, 185(8), 1493-505 (English) **1984.**
CODEN: MACEAK. ISSN: 0025-116X.

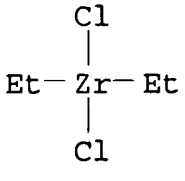
AB The effect of some **metallocenes** such as ferrocene [102-54-5], nickelocene [1271-28-9], and cobaltocene (I) [1277-43-6], on the vinyl polymn. initiated with bis(Et acetoacetato)copper(II) (II) [14284-06-1] was investigated. I exerted a markedly accelerating effect on the polymn. of methyl methacrylate (III) [80-62-6] with II. The polymn. of III with I-II system at 50° was affected by the solvent used. The results of copolymn. of III with styrene and the effect of hydroquinone on the polymn. of III with I-II showed that the polymn. proceeds via a radical mechanism. The polymn. of III with I-II was studied kinetically in acetone. The overall activation energy of the polymn. was calcd. to be 20.6 kcal/mol. This value was somewhat higher than that (17.6 kcal/mol) obtained for the polymn. of III with II alone. The polymn. rate (Rp) is represented by the equation: Rp = k[I]0.5[II]0.2[III]1.3. The high order in monomer concn. suggests a participation of the monomer in the initiation process. This is supported by the examn. of the ESR spectrum of the system I-II-III-acetone, where redn. of Cu(II) to Cu(I) occurs. To elucidate the initiation mechanism, the spin trapping technique was applied to the system I-II-Me acrylate. From these results, an initiation mechanism for the binary initiator system I-II is proposed and discussed.

IT **2247-00-9 92212-70-9**
(effect of, on bis(acetoacetato)copper polymn. catalyst for Me methacrylate)

RN 2247-00-9 ZCA
CN Titanium, dichlorodiethyl-, (T-4)- (9CI) (CA INDEX NAME)



RN 92212-70-9 ZCA
CN Zirconium, dichlorodiethyl-, (T-4)- (9CI) (CA INDEX NAME)



CC 35-3 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 67
IT 102-54-5 1271-28-9 **2247-00-9 92212-70-9**
(effect of, on bis(acetoacetato)copper polymn. catalyst for Me methacrylate)
IT 14284-06-1
(polymn. catalysts, for Me methacrylate, **metallocene** effect on)

=> D L21 1-27 TI

L21 ANSWER 1 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Catalyst systems for polymerization of olefins and stereoregular polymerization of alpha-olefins via metallacyclic intermediates

L21 ANSWER 2 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Diastereoselective addition of methylmetal reagents to 2-methylaldehydes

L21 ANSWER 3 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Natural products via Reetz chemistry synthesis of (±)-cuparene

L21 ANSWER 4 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Synthetic Utility of Organometallic Reagents Derived from Group IV Metal Tetrachlorides and CH3Li. A Direct Synthesis of 2-(2-Keto-1-alkylidene)tetrahydropyrroles from 4-Alkynylamines and Acyl Cyanides

L21 ANSWER 5 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Novel Synthesis of Unbridged, Sterically Substituted Zirconocene Dichlorides from Fulvenes and Dialkylzirconium Dichlorides via Zirconium(IV) Hydride Transfer

L21 ANSWER 6 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Application of the Reetz reagent, dichlorodimethyltitanium, to develop sterically congested quaternary centers. The synthesis of herbertene

L21 ANSWER 7 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI X+ transfer from the halonium ions of adamantylideneadamantane to acceptor olefins. The possibility of chiral induction in the transfer process

L21 ANSWER 8 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Highly diastereoselective addition of organometallics to novel chiral α-ketoamides of (S)-2-methoxymethylindoline

L21 ANSWER 9 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Studies on fused pyrimidine derivatives. XI. A facile generation and stereoselective cycloaddition reactions of 5,6-dihydro-5,6-bis(methylene)-2,4(1H,3H)-pyrimidinedione intermediate

L21 ANSWER 10 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Stereocontrolled addition reaction of organometallics to chiral α-keto amides

L21 ANSWER 11 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Diastereofacial-controlled addition reaction of alkoxymethyl ketones modified by (2R,4)-2,4-pentanediol with organometallics

L21 ANSWER 12 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Chelation vs. non-chelation control in addition reactions of ethylmetallic reagents to acrolein dimer

L21 ANSWER 13 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Geminal dimethylation of acetylbenzenes for preparation of tert-butylbenzene derivatives. Simplified synthesis of 1,3-ditert-butylbenzene

L21 ANSWER 14 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Direct geminal dimethylation of aromatic aldehydes with dichlorodimethyltitanium

L21 ANSWER 15 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Direct geminal dimethylation of ketones and exhaustive methylation of carboxylic acid chlorides using dichlorodimethyltitanium

L21 ANSWER 16 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Radical reactions of organic derivatives of transition metals

L21 ANSWER 17 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Nucleophilic cleavages of acetals using organotitanium reagents. A new synthesis of chiral alcohols

L21 ANSWER 18 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Radical reactions in a coordination sphere of methyl derivatives of titanium

L21 ANSWER 19 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Direct geminal dialkylation of ketones using organotitanium reagents. A simple entry into synthetic tetrahydrocannabinoids

L21 ANSWER 20 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Direct geminal dimethylation of ketones using dimethyltitanium dichloride

L21 ANSWER 21 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Carbon-carbon bond formation using alkyltitanium(IV) compounds

L21 ANSWER 22 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Interaction of nitric oxide with paramagnetic and diamagnetic alkyls of titanium, zirconium, vanadium, niobium, and tantalum

L21 ANSWER 23 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Chemo- and diastereoselective addition of alkyl and aryl titanium(IV) compounds to aldehydes and ketones

L21 ANSWER 24 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Chemoselective and position-specific methylation of tert-alkyl halides with methyltitanium(IV) chlorides

L21 ANSWER 25 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Compensation effect in the decomposition of σ-organotitanium compounds

L21 ANSWER 26 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Reactions of organotitanium compounds with potentially bidentate alkenyloxo and related ligands

L21 ANSWER 27 OF 27 ZCA COPYRIGHT 2007 ACS on STN
TI Thermal decomposition of methyl titanium chlorides

=> D L21 5,26 CBIB ABS HITSTR HITRN

L21 ANSWER 5 OF 27 ZCA COPYRIGHT 2007 ACS on STN
130:311891 Novel Synthesis of Unbridged, Sterically Substituted Zirconocene Dichlorides from Fulvenes and Dialkylzirconium Dichlorides via Zirconium(IV) Hydride Transfer. Eisch, John J.; Owuor, Fredrick A.; Shi, Xian (Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY, 13902-6016, USA). Organometallics, 18(9), 1583-1585 (English) **1999.** CODEN: ORGND7. ISSN: 0276-7333. OTHER SOURCES: CASREACT 130:311891. Publisher: American Chemical Society.
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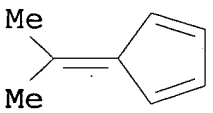
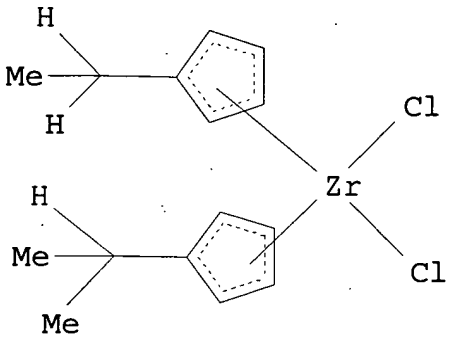


I



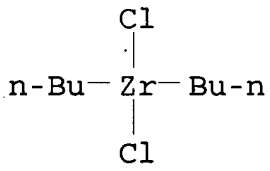
II

AB Unbridged, sterically substituted zirconocene dichlorides can be prepd. in high yields by the interaction of a dialkylzirconium dichloride with 2 equiv of the appropriate fulvene in hydrocarbon medium with alkene displacement. For example, Bu2ZrCl2 was added to a toluene soln. of I and heated at reflux for 8 h, producing II in 92% yield. The requisite dialkylzirconium dichloride can readily be produced by the alkylation of ZrCl4 in hydrocarbon media with 2 equiv of an alkyllithium reagent. Generating the R2ZrCl2 reagents in hydrocarbon media permits their use as hydrozirconating agents for a variety of polar unsatd. org. substrates.

IT **223594-30-7**
(reaction with polar unsatd. org. substrates)

RN 223594-30-7 ZCA

CN Zirconium, dibutyldichloro-, (T-4)- (9CI) (CA INDEX NAME)



IT **223594-30-7**
(reaction with polar unsatd. org. substrates)

L21 ANSWER 26 OF 27 ZCA COPYRIGHT 2007 ACS on STN

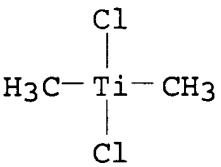
81:130331 Reactions of organotitanium compounds with potentially bidentate alkenyloxo and related ligands. Clark, Robin J. H.; Coles, Michael A. (Christopher Ingold Lab., Univ. Coll., London, UK). Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (14), 1462-7 (English) **1974** . CODEN: JCDTBI. ISSN: 0300-9246.

AB LH [L = CH2:CH(CH2)2Og with BuLi and TiCl4, and with [(cp)2TiCl2] (cp = η-cyclopentadienyl) gave [TiCl3Lg (I) and [(cp)2TiClLg (II), resp. II with MeL gave [(cp)2-TiMeLg. The 1:1 complex of TiCl4 with MeO(CH2)2CH:CH2 is a Cl-bridged dimer contg. 6-coordinate Ti, [TiCl4[MeO(CH2) 2-CH:CH2]]2 (III). NMR data showed insufficient variation in the chem. shifts of the olefinic protons in III and in I and its 6-coordinate derivs. to imply Ti-olefin bonding. Me2TiCl2 and I gave 1:1 adducts with tetramethylethylenediamine.

IT **35739-70-9**
(reactions of, with tetraethylammonium chloride and tetramethyldiaminoethane)

RN 35739-70-9 ZCA

CN Titanium, dichlorodimethyl-, (T-4)- (9CI) (CA INDEX NAME)



IT **35739-70-9**
(reactions of, with tetraethylammonium chloride and tetramethyldiaminoethane)

=> D L25 1-72 TI

L25 ANSWER 1 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization processes using volatile hydrofluorocarbon diluents

L25 ANSWER 2 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Copolymers with new sequence distributions and blends

L25 ANSWER 3 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Copolymers substantially free of long chain branching and blends

L25 ANSWER 4 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization processes utilizing bayonet cooled slurry reactor systems and diluents including hydrofluorocarbons

L25 ANSWER 5 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization processes utilizing a hydrofluorocarbon diluent

L25 ANSWER 6 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization processes utilizing a hydrofluorocarbon diluent

L25 ANSWER 7 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Specific solvent effect on R2ZrCl2 (R = butyl, ethyl) reactivity, a density functional study

L25 ANSWER 8 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Asymmetric Diels-Alder reactions of N-sulfinyl dienophiles using chiral Ti(IV) Lewis acids

L25 ANSWER 9 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Asymmetric N-sulfinyl dienophile Diels-Alder cycloadditions using chiral Ti(IV)-based Lewis acids

L25 ANSWER 10 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Dimethyl titanium dichloride: A high active catalyst for the ring opening metathesis polymerization

L25 ANSWER 11 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Preparation and structure of methyltitanium compounds

L25 ANSWER 12 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI On the relation between π bonding, electronegativity, and bond angles in high-valent transition metal complexes

L25 ANSWER 13 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Method for producing aerogel composites

L25 ANSWER 14 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Core distortions in metal atoms and the use of effective core potentials

L25 ANSWER 15 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Organotitanium-induced stereoselective alkylative endo-cleavage of benzyl pentopyranosides

L25 ANSWER 16 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI On the Nature and Incidence of β-Agostic Interactions in Ethyl Derivatives of Early Transition Metals: Ethyltitanium Trichloride and Related Compounds

L25 ANSWER 17 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Titanium and zirconium neopentyl chloro complexes, MNpxCl4-x (x = 1-4)

L25 ANSWER 18 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Deviations from idealized geometries. Part 4. Approximately tetrahedral molecules of form MX2Y2 studied by SCF and MP2 localized orbital calculations

L25 ANSWER 19 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Deviations from idealized geometries. Part 3. Approximately tetrahedral molecules of form MX2Y2 studied by SCF and MP2 calculations

L25 ANSWER 20 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Infrared Spectrum and Structure of Me2TiCl2 and Quantum Mechanical Calculations of Geometries and Force Fields for MeTiCl3 and Me2TiCl2

L25 ANSWER 21 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Molecular Structure of Dimethyldichlorotitanium(IV) by Gas-Phase Electron Diffraction, IR and NMR Spectroscopies, and Density Functional Theory Calculations. Unexpected Distortion from Tetrahedral Coordination Geometry

L25 ANSWER 22 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI NMR Data of Methyltitanium Trichloride and Related Organometallic Compounds. A Combined Experimental and Theoretical Study of MenXCl4-n (n = 0-4; X = C, Si, Sn, Pb, Ti)

L25 ANSWER 23 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization catalyst for polymerization of polyisocyanates to nylon 1

L25 ANSWER 24 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Theoretical studies of organometallic compounds. I. All electron and pseudopotential calculations of methyltitanium chlorides [Ti(CH3)nCl4-n] (n = 0-4)

L25 ANSWER 25 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Storage-stable silicon alkoxide coatings

L25 ANSWER 26 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Transformations of ethyltitanium trichloride under the action of alkylaluminum compounds and unsaturated hydrocarbons according to IR absorption data

L25 ANSWER 27 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Charge-controlling agent for liquid electrostatographic developer

L25 ANSWER 28 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI The chemistry of transition metal alkyl compounds. XLI. Preparation and thermolysis products of methyltitanium halides

L25 ANSWER 29 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Olefin polymerization catalyst

L25 ANSWER 30 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Stereoselective addition of organotitanium reagents to carbonyl compounds

L25 ANSWER 31 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polyolefins

L25 ANSWER 32 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Organo(transition metal) compounds

L25 ANSWER 33 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Plastic-supported electrode plates for liquid crystal display devices

L25 ANSWER 34 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Red-colored polyesters

L25 ANSWER 35 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Catalyst for polymerization of α-monoolefins

L25 ANSWER 36 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Ruthenium catalyzed process for acetaldehyde and ethanol

L25 ANSWER 37 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI NMR and gas-liquid chromatographic studies of the interaction of components of a catalytic system

L25 ANSWER 38 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Geminal dialkylation of ketones with Grignard compounds and methyltitanium(IV) chlorides

L25 ANSWER 39 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization catalyst component

L25 ANSWER 40 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Enameled articles with metallic-like pattern

L25 ANSWER 41 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Conversion of conjugated dienes to diacyloxy olefins

L25 ANSWER 42 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Catalyst for polymerization, copolymerization, and oligomerization of olefins and diolefins

L25 ANSWER 43 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI 1-Butene

L25 ANSWER 44 OF 72 ZCA COPYRIGHT 2007 ACS on STN

TI Reactions of triphenylmethyl radical with complex organometallic catalysts

L25 ANSWER 45 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Electronic structure and spectra of titanium tetrachloride and the methyltitanium chlorides

L25 ANSWER 46 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Rheological properties of high-density polyethylene prepared on a dissolved complex catalyst

L25 ANSWER 47 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Ester plasticizers

L25 ANSWER 48 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Effect of donor ligands on the nature of the titanium-carbon σ-bond

L25 ANSWER 49 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Copolymerization of ethylene with propylene of a soluble catalytic system bis(cyclopentadienyl)titanium dichloride-diethylaluminum chloride in ethyl chloride

L25 ANSWER 50 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization of isoprene in the presence of allyl complexes of transition metals

L25 ANSWER 51 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Catalytic preparation of macromolecular formaldehyde polymers

L25 ANSWER 52 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Infrared and nuclear magnetic resonance spectra of methyl titanium halides

L25 ANSWER 53 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Kinetics of the polymerization of styrene with a soluble Ziegler-Natta catalyst

L25 ANSWER 54 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerizing α-olefins

L25 ANSWER 55 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Cellular polyurethanes employing tertiary amines and organometallic compounds as catalyst system

L25 ANSWER 56 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI High-molecular-weight polyolefins

L25 ANSWER 57 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polyisobutylene

L25 ANSWER 58 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Linear polynaphthofurans

L25 ANSWER 59 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Configuration in polymerization of ethylene or acetylene in the presence of a Ziegler catalyst

L25 ANSWER 60 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Molecular weights and physicomechanical properties of polyethylene obtained by the system (C5H5)2TiCl2-Et2AlCl

L25 ANSWER 61 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Mechanism of N fixation in the (C5H5)2TiCl2-C2H5MgBr system

L25 ANSWER 62 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Process for purifying liquids or dissolved compounds of halides, halide hydrides, alkyls, and alkoxyls

L25 ANSWER 63 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Kinetics of the polymerization of styrene-α-d and (or) styrene by homogeneous catalysis. II

L25 ANSWER 64 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization of deuterioethylene on the homogeneous catalytic system Et2TiCl2 + Me2AlCl

L25 ANSWER 65 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Double-bond opening and isomerization and hydrogen-exchange reactions in the polymerization of dideuterioethylene

L25 ANSWER 66 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Low-pressure preparation of diamond-structured carbon

L25 ANSWER 67 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI The infrared spectra of trimethyl aluminum, dimethyl aluminum chloride, methyl aluminum dichloride, methyl titanium trichloride, dimethyl titanium dichloride, and some deuterium derivatives

L25 ANSWER 68 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Coordination polymerization of olefins. Catalyst studies. I. The infrared spectroscopic investigation of the systems (CH3)3Al-TiCl4 and (CH3)2Zn-TiCl4

L25 ANSWER 69 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Dimethyltitanium dichloride

L25 ANSWER 70 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI 2-Methyl-1-butene and trialkylaluminum compounds

L25 ANSWER 71 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Polymerization of ethylene with alkyltitanium halide catalysts

L25 ANSWER 72 OF 72 ZCA COPYRIGHT 2007 ACS on STN
TI Alkyltitanium halides

=> D L25 12,49,60,61 CBIB ABS HITSTR HITRN

L25 ANSWER 12 OF 72 ZCA COPYRIGHT 2007 ACS on STN
132:127975 On the relation between π bonding, electronegativity, and bond angles in high-valent transition metal complexes. Kaupp, Martin (Institut fur Anorganische Chemie Universitat Wurzburg, Wurzburg, D-97074, Germany). Chemistry--A European Journal, 5(12), 3631-3643 (English) **1999.** CODEN: CEUJED. ISSN: 0947-6539. Publisher: Wiley-VCH Verlag GmbH.

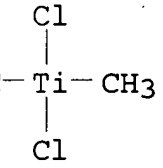
AB Ligand-to-metal π bonding is important for the understanding of bond angles in d0 transition metal complexes. This is demonstrated by d. functional calcns. on a no. of model complexes, combined with natural bond orbital and natural localized MO analyses. Analyses of the simple model systems ScF2+ and ZrO2 indicate a complicated dependence of π bonding on bond angle. In particular, in-plane π bonding exhibits a nonuniform dependence, whereas out-of-plane π bonding shows a more regular behavior. This may be understood from the nodal properties of the relevant metal d orbitals. The net π bonding behavior then depends sensitively on the donor properties of the ligands. While π bonding appears to favor the bent equil. structure for the "strong π-donor case" ZrO2, it is more efficient at a linear structure for the "weak π-donor case" ScF2+. Similar considerations come into play for more complicated species, exemplified by MX2Y2 model complexes. Thus, the "inverse Bent's rule structures" of TiCl2(CH3)2 and TiCl2H2 are related to the improved in-plane π(Ti-Cl) bonding at larger Cl-Ti-Cl angles. In contrast, for CrO2F2 or MoO2F2, the angular dependences of the strong in-plane and out-of-plane components of π(M-O) bonding compensate each other partially, and the O-M-O angles appear to be dominated by the σ-bonding framework. When introducing a strong σ-bonding ancillary ligand, as in CrO2H2, the net π bonding does again seem to favor larger angles. Electronegativity effects on bond angles have been probed by studying heteroleptic complexes without significant π bonding. "Inverse structures" are found for complexes like TiH2(CF3)2 or Ti(SiH3)2(CH3)2, that is the smaller angles are those between the less electroneg. ligands.

Hybridization analyses indicate less d character for these bonds. The interpretation is complicated by the fact that even the structure for the silicon analog of the latter complex violates Bent's rule. In general, Bent's rule appears to be less useful for d0 transition metal complexes than for main group compds., in part due to the much larger importance of π bonding for the former.

IT **35739-70-9**
(relation between π bonding, electronegativity, and bond angles in high-valent transition metal complexes studied theor.)

RN 35739-70-9 ZCA

CN Titanium, dichlorodimethyl-, (T-4)- (9CI) (CA INDEX NAME)



IT **35739-70-9**
(relation between π bonding, electronegativity, and bond angles in high-valent transition metal complexes studied theor.)

L25 ANSWER 49 OF 72 ZCA COPYRIGHT 2007 ACS on STN

78:58879 Copolymerization of ethylene with propylene of a soluble catalytic system bis(cyclopentadienyl)titanium dichloride-diethylaluminum chloride in ethyl chloride. Belov, G. P.; Belova, V. N.; Raspopov, L. N.; Kissin, Y. V.; Brikenshtein, Kh. A.; Chirkov, N. M. (Inst. Chem. Phys., Chernogolovka, USSR). Polymer Journal (Tokyo, Japan), 3(6), 681-9 (English) **1972.** CODEN: POLJB8. ISSN: 0032-3896.

AB For the copolymn. of 0.2-24.3% propylene (I) [115-07-1] with ethylene (II) [74-85-1] in the presence of diethyltitanium dichloride [**2247-00-9**] and diethylaluminum [871-27-2] in EtCl, the II reactivity ratio at 20.deg. was 8.7+-0.5. Increasing the amt. of I increased the copolymn. rate, melt index, and elongation at break, while the rigidity and yield strength were reduced. A cationic propylene oligomerization was obsd. after the copolymn. reaction.

L25 ANSWER 60 OF 72 ZCA COPYRIGHT 2007 ACS on STN

66:29219 Molecular weights and physicomechanical properties of polyethylene obtained by the system (C5H5)2TiCl2-Et2AlCl. Belov, G. P.; Raspopov, L. N.; Lisitskaya, A. P.; Tsvetkova, V. I.; Chirkov, N. M. (Inst. Chem. Phys., Moscow, USSR). Vysokomolekulyarnye Soedineniya, 8(9), 1568-73 (Russian) **1966.** CODEN: VMSDA8. ISSN: 0042-9368.

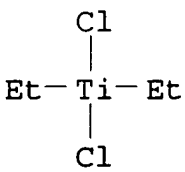
AB The effects of reaction conditions on the mol. wt. and on some

physicomech. properties of polyethylene obtained in EtCl by using the above homogeneous catalyst system were studied. The following parameters were investigated: concn. of monomer and catalysts, temp., and O and H2O content of the monomer. Increasing the pressure of the monomer led to a linear increase in the mol. wt. of the polymer, as detd. by characteristic viscosity of the soln. in 1,2,3,4-tetrahydronaphthalene at 130°. In the range of reaction conditions studied, the effect of termination and chain-transfer reactions was negligible, and the mol. wt. of the product could be controlled within wide limits by the pressure of the monomer in the reaction zone. Increasing the initial concn. of Et2AlCl (I) from 2.0 + 10-3 to 1.0 + 10-2 mole/l. while keeping the initial concn. of (C5H5)2TiCl2 (II) const. at 0.2 + 10-3 mole/l. led to a redn. in the mol. wt. from 91,000 to 46,000. Similarly, the mol. wt. of the polymer decreased when the concn. of II was increased, while that of I was kept const., and also when the overall catalyst concn. was increased whilst the I/II ratio was maintained at 10:1. As the reaction temp. was increased from 10 to 40°, the mol. wt. dropped from 211,000 to 35,000. The relation between mol. wt. and temp. was satisfactorily described by the equation: M = 3.71 + 10-4 exp (10,000/RT). Increasing the O content of the monomer from 100 to 1490 ppm. led to a redn. of mol. wt. from 83,000 to 40,700, while an increase in the H2O content of the monomer from 10 to 620 ppm. reduced the mol. wt. from 110,000 to 35,000. Tensile properties of polymers lying in a wide range of characteristic viscosities (from 0.87 to 8.25 dl./g.) were measured. Specimens having characteristic viscosities <1.10 dl./g. were brittle and failed either before reaching the yield stress or on formation of the neck. Further increases in characteristic viscosity resulted in redn. of the portion of the stress-strain curve corresponding to neck growth, until, at characteristic viscosities >8.0 dl./g., the peak on the stress-strain curve disappeared and the specimens deformed without forming a neck. Curves of yield and ultimate strengths, ultimate elongation, and elongation of the neck as functions of the characteristic viscosity of the polymer are presented.

IT **2247-00-9**
(catalysts from chlorodiethylaluminum and, for polymn. of ethylene)

RN 2247-00-9 ZCA

CN Titanium, dichlorodiethyl-, (T-4)- (9CI) (CA INDEX NAME)



IT **2247-00-9**
(catalysts from chlorodiethylaluminum and, for polymn. of ethylene)

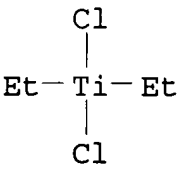
L25 ANSWER 61 OF 72 ZCA COPYRIGHT 2007 ACS on STN
64:36008 Original Reference No. 64:6686a-c Mechanism of N fixation in the (C5H5)2TiCl2-C2H5MgBr system. Nechiporenko, G. N.; Tabrina, G. M.; Shilova, A. K.; Shilov, A. E. Doklady Akademii Nauk SSSR, 164(5), 1062-4 (Russian) **1965.** CODEN: DANKAS. ISSN: 0002-3264.

AB Gaseous products of the reaction between Et2TiCl2 and EtMgBr contain C2H6 and C2H4. When C2D5MgBr is used as a reducing agent, C2H6 contains chiefly C2D6. The redn. proceeds as follows: Et2M → M + C2H4 + C2H6, where M is the metal atom. Hydrolysis of the reaction products of Et2TiCl2 and EtMgBr leads to formation of H. The mass-spectroscopic analysis of the isotopic compn. of the gas isolated reveals that when D2O is used instead of H2O for hydrolysis, the compds. undergoing hydrolysis are metal hydrides, which indicate an advanced redn. Further studies on the passage of N through the reaction mixt. show no formation of NH3. N is fixed, probably in the form of nitrides, as a result of the reaction between N and Mg or Ti in the nascent state, which is possible in the case of an advanced redn. to the metal. C2H6 and C2H4 analyses are carried out by chromatographic and massspectrometric methods. A mass spectrometer is used for the isotopic analysis of H, D, C2H6, and C2D6 gases.

IT **2247-00-9**, Titanium, dichlorodiethyl-
(system, bromoethylmagnesium-, N fixation in)

RN 2247-00-9 ZCA

CN Titanium, dichlorodiethyl-, (T-4)- (9CI) (CA INDEX NAME)



IT **2247-00-9**, Titanium, dichlorodiethyl-
(system, bromoethylmagnesium-, N fixation in)